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

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Experimental and theoretical studies have been first time performed to investigate the sorption of atrazine as well as the competitive sorption of the coexisting atrazine and chlorpyrifos in solution by wheat straw-derived biochar synthesized at 750 ^{o}C through oxygen-limited method (WS750). The sorption of atrazine by WS750 follows pseudo-second-order and Langmuir models. In separate sorption, WS750 has higher sorption quantity (12.0 mg/g, 0.0556mmol/g) for atrazine than that (18.8 mg/g, 0.0537mmol/g) for chlorpyrifos, being due to that the molecular volume (268.8 Å^3) of atrazine is smaller than that (350.8 Å^3) of chlorpyrifos. In competitive sorption, the sorption quantity of chlorpyrifos by WS750 is 16.5 mg/g (0.0470mmol/g), which is larger than that (7.3 mg/g, 0.034mmol/g) of atrazine. This is from that chlorpyrifos has stronger pi-pi interaction with WS750 (23.68 kcal/mol) and larger lipophilicity (logP = 4.7) than that (22.70 kcal/mol, logP = 2.7) of atrazine. The competitive isotherm sorption of the coexisting atrazine and chlorpyrifos by WS750 can be described well by sheindorf–Rebuhn–Sheintuch equation. This work is helpful to deep understand the sorption of bi-pollutants in water.

1. Introduction

Chlorpyrifos is broad spectrum organophosphate pesticide and atrazine is a kind of triazine herbicide. They are widely used to kill pests and weeds in cropland for obtaining high yield of crop. However, the residuals of chlorpyrifos and atrazine in cropland have been confirmed harmful for living beings and have resulted in serious soil contamination.[1-2] Furthermore, residuals of chlorpyrifos and atrazine can transfer into rivers and lakes from farmland, which are also toxic for some species in water, e.g. frog and fish.[3-4] Many methods have been developed to remove chlorpyrifos and atrazine from water. It has reported that phosphorus-containing pesticides (including chlorpyrifos) can be decomposed by organophosphate hydrolase.[5] Bacterial acquired from the soil can also be used to decompose chlorpyrifos in water.[6] Recent study[7] shows that sulfate radical can effectively degrade atrazine in the presence of humic acid. Photocatalytic material, such as TiO_2, can degrade chlorpyrifos and atrazine into small harmless molecules under light irradiation.[8] Sorption is a common used method to remove the contaminants from water since of its simplicity and low cost.[9] For example, cellulose/graphene composite can adsorb triazine pesticides (including atrazine) and its sorption performance can be easily recovered by washing with organic solvent.[10] Zr-based metal organic framework material can adsorb organophosphorus pesticides in a high efficiency based on the interaction between the Zr–OH groups and phosphoric groups.[11]

Agricultural straws are the residuals from the harvest of agricultural crops, such as wheat, rice. The traditional way of treating straws is to directly burn them in cropland, which has resulted in serious air contamination.[12] For reducing environmental pollution and waste recycling, many efforts have been paid to develop these technologies of recycling straw, in which using straw to produce biochar is the promising one since biochar can be used to soil remediation, carbon dioxide fixation and sorption due to its large surface area and high microporosity.[13] Most of the applications of biochar are related to soil remediation.[13-14] Rice-straw derived biochar can effectively adsorb pentachlorophenol in sediment.[15] Wheat straw derived biochar is used to immobilize chlorobenzenes in soil,[16] to replace peat in soilless substrates,[17] and to adsorb cadmium cation in soil.[18] Recently, biochars are also used as sorbent to remove pesticides from water. Rice husk derived biochar can remove ammonium nitrogen from anaerobic digestate slurry.[19] Corn straw derived biochar is able to adsorb atrazine in water.[20] Wheat straw derived biochar can also work as good sorbent to remove chlorpyrifos from waste water based on our previous study.[21] However, the report using wheat straw derived biochar to remove atrazine from waste water is still not found so far.

Furthermore, most of studies just focus on the sorption of single pollutant from waste water at the present time.[9-10, 19-21] However, pollutants coexist in waste water in real situation. Wang et al have found that the sorption speed of glyphosate by Zr-based metal organic framework is faster than that of glufosinate.[11] Sudhakar et al have reported that the coexisting pesticide hinders the sorption of endosulfan by wood charcoal, being due to the competition of the coexisting molecules for the available sorption sites on wood charcoal surface.[22] Similar experimental phenomenon has also been

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reported by Rajagopalan et al.[23] The sorbent with aromatic structure can selectively absorb benzene over cyclohexane since the driving force of sorption is the pi-pi interaction.[24] Atrazine and chlorpyrifos are used at different time in the field. But, the residuals of atrazine and chlorpyrifos in the field can successively transfer into river. The two pesticides are not easily decomposed in water under natural condition. So, coexistence of atrazine and chlorpyrifos in river is possible. For example, Xu et al have investigated the toxicity of atrazine and chlorpyrifos in combination on the common carp.[25] Lydy et al have found that the presence of atrazine can increases the toxicity of chlorpyrifos on aquatic vertebrates.[26] So far, the competitive sorption of the coexisting atrazine and chlorpyrifos in waste water by sorbent has not been investigated.

Herein, experimental and theoretical studies have been first time performed to investigate the sorption of atrazine and the competitive sorption of the coexisting atrazine and chlorpyrifos in solution by wheat straw derived biochar synthesized at 750 ^{o}C (WS750). The objectives of this work are to: (1) investigate the sorption mechanism of atrazine by WS750; (2) investigate the competitive sorption mechanism of the coexisting atrazine and chlorpyrifos in solution by WS750.

2. Experimental and Computational Sections

2.1 Regents

Wheat straw was acquired from a farm of LiuHe district, Nanjing City, China. Chlorpyrifos (99% grade) was purchased from Chengdu Chemical Reagent Co., Ltd. Atrazine (97% grade) was purchased from TCL company, Japan. Methanol (chromatographic grade) was purchased from the TEDIA company, America. Sodium hydrate (analytical grade), calcium chloride (analytical grade) and hydrochloric acid (HCl, analytical grade) were purchased from the Sinopharm Chemical Reagent limited corporation, P.R. China.

2.2 Preparation of biochar

The procedure using wheat straw to synthesize WS750 was same as that in our previous work.[21] Wheat straw was first washed to remove impurities and dried at 80 ^{o}C, then, the dried wheat straw was crushed into powder with a disintegrator, and followed by passing through a 20 mesh sieve. After that, wheat straw powder was filled the full crucible, which was closed with the cover. Then, the crucible with cover was put into furnace and heated at 750 ^{o}C for two hours. The heating rate was 10 ^{o}C/min. The obtained biochar sample was first washed with 1 mol L^{-1} HCl to remove soluble minerals, and then washed with deionized water to neutral state. The sample was named as WS750. Same procedure was adopted to synthesize WS250, WS350, WS450 WS550 and WS650 samples, in which the heating temperatures for these samples were 250 ^{o}C, 350 ^{o}C, 450 ^{o}C, 550 ^{o}C and 650 ^{o}C, respectively.

2.3 Preparation of atrazine and chlorpyrifos solution

The solubility of atrazine in water was low (33.0 mg L^{-1}). So, a stock solution of atrazine (10 g L^{-1}) was first prepared by dissolving it in methanol. The stock solution was diluted into specific concentrations with 0.005 mol L^{-1} $CaCl_2$ solution for sorption test. The purpose of adding $CaCl_2$ in solution was to keep a constant ionic strength.[27] The volume ratio between methanol and water in the diluted solution was maintained below 1:1000 to minimize the cosolvent effect. [21, 27]

Same procedure was also adopted to prepare chlorpyrifos solution since the solubility of chlorpyrifos in water was low as well (1.20 mg L^{-1}). Firstly, a stock solution of chlorpyrifos (2.5 g L^{-1}) was prepared by dissolving it in methanol. Then, the stock solution was diluted into specific concentrations with 0.005 mol L^{-1} $CaCl_2$ solution for sorption test. The volume ratio between methanol and water in the diluted solution was maintained below 1:1000 to minimize the cosolvent effect. [21, 27]

2.4 Characterization of the samples

Surface area of WS750 sample was determined with HD88, ASAP2020 micropore analyzer (USA). Zeta potential of WS750 was determined with Zetasizer Nano ZS (UK). The components of ash from WS750 were analysed with Electronic Differential System method (EDS, S-3400N II, Japan). The Fourier transform infrared spectrum (FTIR) of WS750 sample was acquired using Nexus 870 FT-IR instrument. The valence state of C1s in WS750 was studied through X-ray Photoelectron Spectroscopy (PHI 5000 VersaProbe, Japan).

The concentration of atrazine was determined using High Performance Liquid Chromatography (HPLC, Waters e2696, USA) with a UV detector (Waters 2489) at a wavelength 230 nm. The parameters of column were listed as following: Bridge, 5μm, 4.6×150 mm C18. The used mobile phase was the mixture of methanol and water (80:20 V:V), while the flow rate was 1mL min^{-1}. The temperature of column was kept at 20 ^{o}C. The injected sample volume was 20 μL and the retention time was 2.69 min. The detection limit of atrazine was 0.25 μg L^{-1} with a signal-to-noise ratio of 3:1. The sorption quantity of atrazine was acquired through HPLC-external standard method, in which the sorption quantity of atrazine by WS750 was determined by using the quantity of atrazine before sorption to subtract the residual quantity of atrazine in the supernatant after sorption. A series of experiments had been done to make sure that the acquired sorption quantity of atrazine by WS750 through HPLC-external standard method was accurate. According Fig.S1, the HPLC peak of atrazine had a good linear correlation with the concentration of atrazine since R^2 was 0,9997. From Fig. S2, the HPLC peaks of atrazine at starting time and 72 hours later were identical, implying that atrazine was stable under sorption conditions.

The concentration of chlorpyrifos was determined using High Performance Liquid Chromatography (HPLC, Waters e2696, USA) with a UV detector (Waters 2489) at a wavelength 300 nm. The parameters of column were listed as following: Bridge, 5μm, 4.6×150 mm C18. The used mobile phase was the mixture of methanol and water (90:10 V:V), and the flow rate was 1ml min^{-1}. The temperature of column was kept at 25^{o}C. The injected sample volume was 100 μL and the retention time was 3.9 min. The detection limit of chlorpyrifos was 0.36 μg L^{-1} with a signal-to-noise ratio of 3:1. The sorption quantity of chlorpyrifos was acquired through HPLC-external standard method as well. The HPLC peak of chlorpyrifos had a good linear correlation with the concentration of chlorpyrifos since R^2 is 0,9991 (Fig S3). Furthermore, chlorpyrifos was stable in the sorption process since the HPLC peaks of chlorpyrifos at starting time and 72 hours later were identical (Fig S4).

2.5 Sorption experiments

2.5.1 Sorption experiments of atrazine by WS250, WS350, WS450 WS550, WS650 and WS750 samples

For investigating the effect of carbonization degree on the sorption of atrazine, the sorptions of atrazine by WS250, WS350, WS450, WS550, WS650 and WS750 samples were investigated. For these sorption experiments, the concentration of atrazine was 5.80 mg L^{-1}. The detailed sorption procedure was as following: 5.0 mg biochar sample was weighted and put into the EPA bottle. The bottle cap had teflon gasket for avoiding the sorption for atrazine. EPA bottle was purchased from Shanghai ANPEI Instrument Co. Ltd, China. Then, atrazine solution (5.80 mg L^{-1}) was filled into the EPA bottle, followed by rotation of 96 hours with the rotation rate (70 r/min) at room temperature under dark condition. Three parallel experiments were performed for each sorption test. After sorption experiments were finished, the supernatants in these EPA bottles were taken to determine the residual atrazine quantity, then followed by determining the sorption quantities of atrazine by WS250, WS350, WS450, WS550, WS650 and WS750 samples with HPLC-external standard method.

2.5.2 The pH effect on the sorption of atrazine by WS750

For investigating the effect of pH on the sorption of atrazine by WS750, the pH of the diluted atrazine solution was adjusted to 4.9, 6.1, 7.1, 8.3, and 9.1, respectively. The concentration of atrazine is 5.80 mg L^{-1}. The sorption procedure was same as that mentioned in 2.5.1 section. The sorptions of atrazine by WS750 in strong basic and acidic conditions were not considered since atrazine was just stable in slightly acidic and basic conditions.

2.5.3 Sorption experiment of atrazine by the inorganic component in WS750

10g WS750 sample was put into crucible and was heated at 800 ^{o}C for two hours without cover. The ash in the bottom of crucible was collected for investigating its sorption ability for atrazine. The concentration of atrazine in this sorption experiment was 5.80 mg L^{-1} and the sorption procedure was same as that mentioned in 2.5.1 section.

2.5.4 The effect of $CaCl_2$ concentration on the sorption of atrazine by WS750

For investigating the effect of $CaCl_2$ concentrations on the sorption of atrazine by WS750, the concentrations of $CaCl_2$ were changed from 0.005 mol L^{-1}, 0.010 mol L^{-1}, 0.050 mol L^{-1} to 0.100 mol L^{-1} in the diluted atrazine solution. The concentration of atrazine was 5.80 mg L^{-1}. The sorption procedure was same as that mentioned in 2.5.1 section.

2.5.5 Kinetics sorption of atrazine by WS750

During the kinetics sorption experiment, the concentration of atrazine was 5.80 mg L^{-1} and the sorption procedure was same as that mentioned in 2.5.1 section. The supernatants were collected at time intervals of 0.5, 1, 2, 4, 6, 8, 10, 12, 18, 24, 30, 36, 48, 56, 72, 96 and 120 hours of rotation to determine the sorption quantities of atrazine by WS750 at different time with HPLC-external standard method.

2.5.6 Isotherm sorption of atrazine by WS750

A series of atrazine solutions with concentration ranged from 2.80 mg L^{-1} to 8.70 mg L^{-1} were prepared to investigate the isotherm sorption of atrazine by WS750. The procedure of atrazine sorption experiment was same as that mentioned in 2.5.1 section.

2.5.7 Recycle experiment for the sorption of atrazine by WS750

The sorption procedure was same as that mentioned in 2.5.1 section. The concentration of atrazine is 5.8 mg L^{-1} and the amount of WS750 is 5 mg. Three parallel experiments were performed for the sorption of atrazine by WS750. After the sorption experiment was finished, WS750 was collected and washed with methanol, then followed by the reuse of the collected WS750 to adsorb atrazine. This procedure was repeated three times.

2.5.8 Sorption experiment of chlorpyrifos by WS750

For comparing the sorption effect of chlorpyrifos over atrazine by WS750, the sorption of chlorpyrifos by WS750 was done as well. For this sorption experiment, the concentration of chlorpyrifos was 1.12 mg L^{-1} (0.0032 mmol L^{-1}) and the amount of WS750 was 2.5 mg. The procedure of sorption experiment was same as that mentioned in 2.5.1 section. This sorption experiment was carried out in summer, in which the room temperature was about 30 ^{o}C. This was different from that in our previous work,[21] in which the sorption experiment was carried out in winter and the room temperature was about 5 ^{o}C.

2.5.9 Sorption experiment of atrazine by WS750

For comparing the sorption effect of chlorpyrifos over atrazine by WS750, the sorption of atrazine by WS750 was done as well. For this sorption experiment, the concentration of atrazine was 0.69 mg L^{-1} (0.0032 mmol L^{-1}) and the amount of WS750 was 2.5 mg. The procedure of sorption experiment was same as that mentioned in 2.5.1 section.

2.5.10 Competitive kinetics sorption of the coexisting atrazine and chlorpyrifos in solution by WS750

Firstly, stock solution containing atrazine and chlorpyrifos was prepared by dissolving a certain amount of atrazine and chlorpyrifos in methanol, in which the concentration of atrazine was 1.5 g L^{-1} (0.007 mol L^{-1}), and the concentration of chlorpyrifos was 2.5 g L^{-1} (0.007 mol L^{-1}). Then, the stock solution was diluted with 0.005 mol L^{-1} $CaCl_2$ solution to make that the concentration of atrazine was 0.69 mg L^{-1} (0.0032 mmol L^{-1}), and the concentration of chlorpyrifos was 1.12 mg L^{-1} (0.0032 mmol L^{-1}). The amount of WS750 was 2.5 mg. The procedure of sorption experiment was same as that mentioned in 2.5.1 section. The supernatants were collected at time intervals of 1, 2, 4, 6, 9, 12, 18, 24, 36, 48, 60, 72 and 96 hours of rotation to determine the sorption quantities of the coexisting chlorpyrifos and atrazine by WS750 at different time with HPLC-external standard method.

2.5.11 Competitive isotherm sorption of the coexisting atrazine and chlorpyrifos in solution by WS750

A series of solutions were prepared to investigate the isotherm sorption of the coexisting atrazine and chlorpyrifos by WS750, in which the concentrations of atrazine were changed from 0.35 mg L^{-1} (0.0016 mmol L^{-1}) to 0.73 mg L^{-1} (0.0034 mmol L^{-1}), while the concentrations of chlorpyrifos were changed from 0.56 mg L^{-1} (0.0016 mmol L^{-1}) to 1.19 mg L^{-1} (0.0034 mmol L^{-1}). The concentrations of atrazine and chlorpyrifos in the mixed solution were same. The sorption procedure was same as that mentioned in 2.5.1 section. The amount of the used WS750 in this experiment was 2.5 mg.

2.5.12 Recycle experiment for the competitive sorption of the coexisting atrazine and chlorpyrifos by WS750

The adsorption procedure was same as that mentioned in 2.5.1 section. The concentration of atrazine is 0.69 mg L^{-1} (0.0032 mmol L^{-1}

^{1}), and the concentration of chlorpyrifos is 1.12 mg L^{-1} (0.0032 mmol L^{-1}). The amount of WS750 is 2.5 mg. Three parallel experiments were performed for the sorption of the coexisting atrazine and chlorpyrifos by WS750. After the sorption experiment was finished, WS750 was collected and washed with methanol, then followed by the reuse of the collected WS750 to adsorb the coexisting atrazine and chlorpyrifos. This procedure was repeated three times.

A brief summary about these experiments in the 2.5 section was provided in Table S1.

2.6 Computational section

For deep understanding the interaction between atrazine, chlorpyrifos and the aromatic structure of WS750, m062x/6-31g(d,p) method [28] in Gaussian 09 program [29] had been adopted to calculate the interaction energies between atrazine, chlorpyrifos and WS750. For atrazine and chlorpyrifos, full atom models were used (Fig. S5). The FTIR and elemental analysis results in our previous work [21] shown that WS750 had highest aromatic degree among WS250-WS750 samples. Furthermore, WS750 had highest sorption quantity for atrazine among WS250-WS750 samples. So, a graphene model containing 70 carbon atoms was constructed to simulate the aromatic surface of WS750, in which these unsaturated carbon atoms at the edge were saturated with hydrogen atoms. This model was named as WSmodel. In addition, FTIR and XPS results also shown that there were O-containing groups on WS750 surface. So, some O-containing groups were also added at the edge of WSmodel (Fig.S6). The molecular volumes of chlorpyrifos and atrazine were calculated as well based on their optimized structures.

All molecular structures were constructed with Gview 5.0 program based on these optimized results. The interaction energy between atrazine and WSmodel was acquired by using the calculated energy of atrazine-WSmodel complex to subtract the calculated energies of atrazine and WSmodel. The interaction energy between chlorpyrifos and WSmodel was acquired in same way.

3 Results and discussions

Firstly, the atrazine sorption quantities of WS250-WS750 samples are compared. Based on Fig.1, the sorption quantities of atrazine increase from WS250 to WS750 samples and WS750 has highest sorption quantity (about 32.0 mg/g) for atrazine in all samples. According to FTIR and elemental analysis results of WS250-WS750

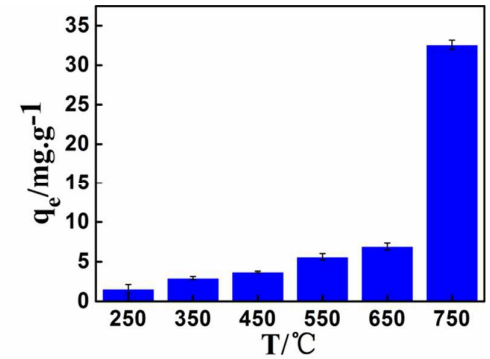

Fig.1 Comparison of atrazine sorption performances of WS250-WS750 samples. The concentration of atrazine is 5.80 mg L^{-1}.

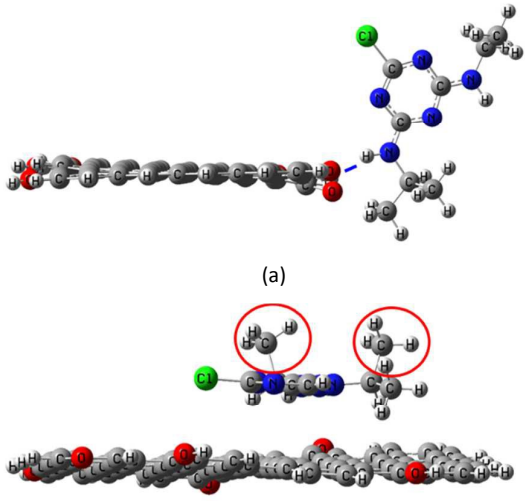

Fig.2 The optimized structures of atrazine-WSmodel complexes formed through (a) hydrogen bonding and (b) pi-pi interaction.

samples in our previous work, [21] WS750 has highest aromatic degree among WS250-WS750 samples. There is also an aromatic ring in atrazine. So, the driving force for atrazine sorption by WS750 is most likely due to the pi-pi interaction between the aromatic ring of atrazine and the aromatic surface of WS750. Theoretical computations have been widely used to deep understand the experimental phenomenons.[30-32] Herein, theoretical computation has also been applied to investigate the interaction between atrazine and WS750. Firstly, the hydrogen bonding interaction between the NH group in atrazine and the O-containing groups in WSmodel is investigated (please see Fig. 2(a)). The H…O distance is 1.79 Å and the interaction energy is 15.2 kcal/mol. Then, the pi-pi interaction energy between the aromatic ring of atrazine and the aromatic surface of WSmodel is calculated, which is 22.7 kcal/mol (please see Fig. 2(b)). This suggests that the driving force of atrazine sorption by WS750 is mainly from the pi-pi interaction between the aromatic ring of atrazine and aromatic surface of WS750. There are two methyl groups in atrazine, which have been surrounded by two red circles (please see the Fig. 2(b)). A new atrazine-WSmodel complex has been designed, in which the two methyl groups point to the aromatic surface of WSmodel (please see Fig. S7). By this way, the interaction between the aromatic ring of atrazine and aromatic surface of WS750 is hindered. The calculated interaction energy between atrazine and WSmodel is just 14.09 kcal/mol. This further supports that the driving force of atrazine sorption by WS750 is mainly from the pi-pi interaction.

WS750 is chosen as model compound to further study its sorption for atrazine since it has the highest sorption quantity for atrazine among all samples. The surface of WS750 has aromatic structure and its BET surface area is 467 m^2 g^{-1}. EDS analysis for ash acquired by heating WS750 at 800 ^{o}C suggests that the inorganic components in WS750 is SiO_2. The zero point zeta potential of

WS750 surface is around pH3.3. The zeta potential of WS750 is positive when the pH of solution is smaller than 3.3, while it is negative when the pH of solution is larger than 3.3. FTIR spectra of WS750 suggests that oxygen-containing groups (such as C-O and C-O-C) exist on WS750 surface. All of these are consistent with that in our previous work.[21] Further XPS characterization for WS750 also supports that the surface of WS750 has aromatic structure and oxygen-containing groups since the C1s peak around 284.3 eV is from the contribution of aliphatic and aromatic carbons (such as C-C, C=C), while the peaks at 285.6, 287.7 and 289.8 eV are assigned to the carbons bonded with oxygen atoms (such as C-O, C=O and C-O-C), respectively (Fig. S8).[33-34]

The influence of pH on the sorption of atrazine by WS750 has been first investigated. According to the full line with these diamond points in Fig. S9, the sorption quantities of atrazine by WS750 gradually decrease with the increased pH values. Based on zeta potential result of WS750, the zeta potential on WS750 surface becomes more negative when pH increases to 9 from 5.[21] Usually, more negative species has weaker interaction with aromatic ring than the less negative species since aromatic ring acts as electron donor in most of case.[35-37] In addition, these N atoms of atrazine can be protonated in acidic condition. This leads to that atrazine is positive in acidic condition and is neutral in basic condition. This explains well why WS750 has stronger sorption for atrazine in low pH condition than that in high pH condition. The pH values at starting time of atrazine sorption by WS750 are 4.9, 6.1, 7.1, 8.3, and 9.1, while they are changed as 5.8, 6.5, 6.8, 7.5 and 7.9 at final time of atrazine sorption by WS750 (please see the dotted line with these triangle points in Fig. S9). These pH changes before and after sorption of atrazine by WS750 are 0.9, 0.4, -0.3, -0.8 and -1.2, respectively. Obviously, WS750 can make both acidic and basic solutions become neutral solution. This buffering effect is most likely due to that these oxygen-containing groups on WS750 surface have interaction with both H^+ and OH^- ions through protonation of O atoms by H^+ and hydrogen bonding between O atoms and OH^-.[13-14, 20]

Then, the influence of the inorganic component on the sorption of atrazine by WS750 is investigated. Based on the sorption result, the inorganic component in WS750 does not adsorb atrazine at all.

The influence of $CaCl_2$ concentration on the sorption of atrazine by WS750 has been investigated since $CaCl_2$ has been added in the diluted atrazine solution for keeping a constant ionic strength.[21, 27] According to Fig. S10, the sorption quantities of atrazine by WS750 decrease with the increased $CaCl_2$ concentrations. This may be due to that these ions (Ca^{2+} and Cl^-) can also occupy the sorption sites on the surface of WS750 through ion…π interaction, [35-38] which results in that the atrazine sorption quantities decrease with the increased $CaCl_2$ concentrations.

The kinetics sorption of atrazine by WS750 has been investigated in this part. The supernatants are taken at 0.5, 1, 2, 4, 6, 8, 10, 12, 18, 24, 30, 36, 48, 56, 72, 96, and 120 hours, respectively. From Fig. 3, the sorption equilibrium nearly arrives after 80 hours of sorption. The equilibrium sorption quantity of atrazine is about 32.0 mg/g. Pseudo-first-order and pseudo-second-order models have been adopted to fit the kinetic sorption data of atrazine by WS750 (Fig. S11 and Table. S2). The experimental sorption quantity is 32.0 mg/g, while the

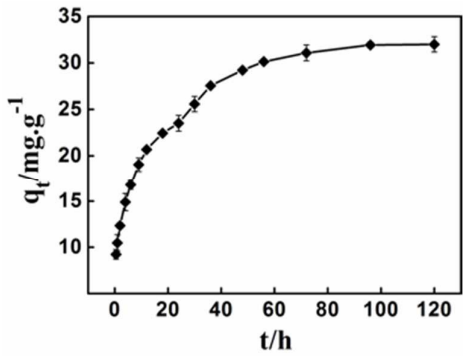

Fig.3 The kinetic sorption of atrazine by WS750. The concentration of chlorpyrifos is 5.80 mg L^{-1}.

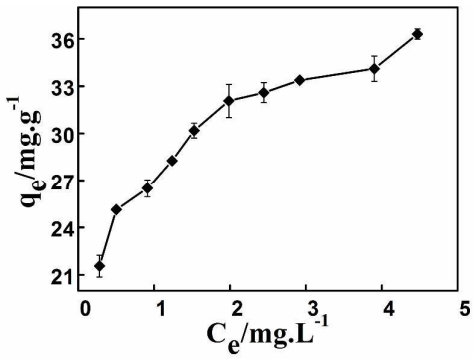

Fig.4 The isotherm sorption of atrazine by WS750. The concentrations of atrazine range from 2.80 mg L^{-1} to 8.70 mg L^{-1}.

sorption quantities from pseudo-first-order model and pseudo-second-order model are 28.734 mg/g and 33.333 mg/g, respectively. Furthermore, the R^2 value from pseudo-second-order model is 0.995, while the R^2 value from pseudo-first-order model is 0.901. Obviously, pseudo-second-order model can give a better description about the kinetic sorption of atrazine by WS750 than pseudo-first-order model.

The isotherm sorption result of atrazine by WS750 is shown in Fig.4. The concentrations of atrazine range from 2.80 mg L^{-1} to 8.70 mg L^{-1} in this sorption experiment. According to Fig. 4, the sorption quantities of atrazine by WS750 increase with the increased atrazine concentrations, and the largest sorption quantify is around 37.0 mg/g. Freundlich and Langmuir models are used to fit the isotherm sorption data of atrazine by WS750. From Fig S12 and Table S3, the correlation coefficient R^2 from Freundlich model is 0.982, while that of R^2 from Langmuir model is 0.996. This suggests that Langmuir model is more suitable to describe the isotherm sorption of atrazine by WS750 than Freundlich model. The N^2 sorption-desorption isotherm of WS750 is shown in Fig S13. When p/p0 is smaller than 0.1, the sorption quantity increases very fast and the sorption speed is fast as well, suggesting that there are lots of micropores in WS750. When p/p0 is larger than 0.1, the sorption quantity increases slowly and hysteresis loop appears, implying that a certain amount mesopore and macropore also exist in WS750. Based on the FTIR, XPS and elemental analysis results, the surfaces (including the inner surfaces of these pores) of WS750 are aromatic. Furthermore, theoretical calculations have confirmed that atrazine

is adsorbed by WS750 through the pi-pi interaction between the aromatic surface of WS750 and the aromatic ring in atrazine. Thus, atrazine is adsorbed on the aromatic surface and in these pores of WS750. Previous works [39-40] have shown that the isotherm sorptions of organic matter on surface and pore of biochar synthesized at 700 °C all follow by Langmuir model.

The recycle sorption experiment of WS750 has also been performed to explore the possibility of using WS750 as sorbent to remove atrazine from waste water. The sorption ability of WS750 is regenerated by washing with methanol. According to Fig. S14, the sorption quantity of WS750 decreases to 22.3 mg/g in the third time from the 31.2 mg/g in the first time. 72% sorption ability of WS750 can be recovered by washing with methanol. The sorption quantity of atrazine by WS750 in the third time is just a little lower than that in the second time. This maybe from that the atrazine adsorbed on WS750 surface and in shallow pore of WS750 is easily to be washed

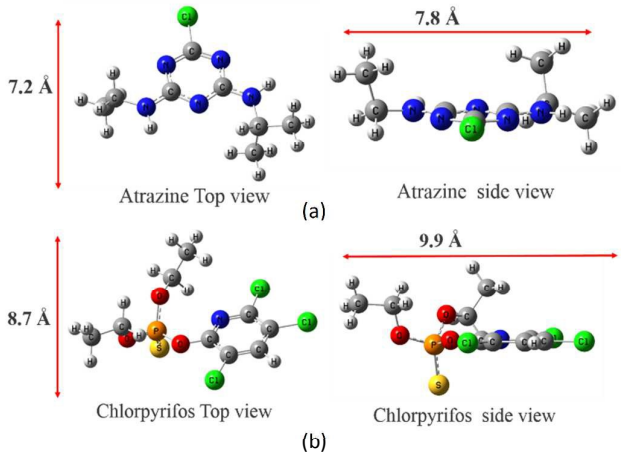

Fig.5 The calculated sizes of (a) atrazine and (b) chlorpyrifos.

off by methanol, but the atrazine adsorbed in the deep pore of WS750 is not easily to be washed off. However, the adsorption quantity (22.3mg/g) is still high and the recovery method is simple. So, it is feasible to use WS750 as sorbent for remove atrazine from waste water.

In real situation, waste water usually contains more than one pollutants. Thus, it is necessary to investigate the sorption of the coexisting atrazine and chlorpyrifos in solution by WS750. The separate sorption of chlorpyrifos by WS750 is first investigated. In this sorption experiment, the used amount of WS750 is 2.5 mg and the concentration of chlorpyrifos is 1.12 mg L^{-1} (0.0032 mmol L^{-1}). After the sorption of 96 hours, the sorption quantity of chlorpyrifos by WS750 is 18.8 mg/g (0.0537 mmol/g). This is a little larger than that in our previous work (16.0 mg/g), [21] being due to that the sorption experiment in the previous work is performed at winter with the room temperature around 5 °C, while the sorption experiment in this work is carried out at summer with the room temperature around 30 °C. Then, the separate sorption of atrazine by WS750 is investigated as well. The used amount of WS750 is 2.5 mg and the concentration of atrazine is 0.69 mg L^{-1} (0.0032 mmol L^{-1}). After the sorption of 96 hours, the sorption quantity of atrazine by WS750 is 12.0 mg/g (0.0556 mmol/g). So, the sorption quantity of atrazine by WS750 is a litter larger than that of chlorpyrifos by WS750 in separate sorption (0.0556 mmol/g vs 0.0537 mmol/g). Abraham parameters, such as volume, pi-pi interaction, are often used to describe the relationship between bio-toxicity and molecular properties.[41] According to Fig. 5, the length and height of atrazine are 7.8 Å and 7.2 Å, while the length and height of chlorpyrifos are 9.9 Å and 8.7 Å. Furthermore, the molecular volume of atrazine is 268.8 $Å^3$, which is smaller than that (350.8 $Å^3$) of chlorpyrifos. Same aromatic area on WS750 surface and same pore volume of WS750 can adsorb more atrazine molecules. Thus, molecular volume can be used as an indicator to assess the sorption quantities of chlorpyrifos and atrazine by WS750 in separate sorption.

Subsequently, a solution containing atrazine and chlorpyrifos is prepared, in which the concentration of atrazine is 0.69 mg L^{-1} (0.0032 mmol L^{-1}), and the concentration of chlorpyrifos is 1.12 mg L^{-1} (0.0032 mmol L^{-1}). The interaction between atrazine and chlorpyrifos is first investigated. The sorption peak of atrazine in

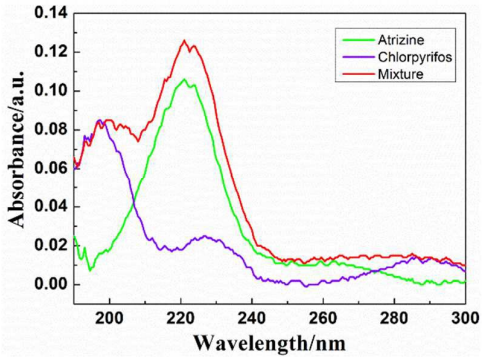

Fig. 6 Uv-vis spectra of atrazine, chlorpyrifos and mixture of atrazine-chlorpyrifos in aqueous solution.

aqueous solution is at 221 nm, while the sorption peak of chlorpyrifos in aqueous solution is at 197 nm (please see Fig.6).[42-43] The Uv peaks of the coexisting atrazine and chlorpyrifos are nearly identical to the overlap of the Uv peaks of atrazine and chlorpyrifos (Fig. 6). This means that atrazine and chlorpyrifos have not obvious interaction in aqueous solution under the experimental condition.

After that, the kinetics sorption of the coexisting chlorpyrifos and atrazine by WS750 are performed. After the sorption of 96 hours (please see Fig.7), the sorption quantity of chlorpyrifos by WS750 is 16.5 mg/g (0.047mmol/g), which is a little lower than the 18.8 mg/g (0.0537mmol/g) in the separate sorption. And the sorption quantity of atrazine by WS750 is 7.3 mg/g (0.034mmol/g), being lower than the 12.0 mg/g (0.0556mmol/g) in the separate sorption. Thus, the sorption of atrazine by WS750 is hindered by the presence of chlorpyrifos, while the sorption of chlorpyrifos is just a little influenced by the presence of atrazine. The sorption quantity of chlorpyrifos by WS750 just decreases a little (from 0.0537mmol/g to0.0470mmol/g), but atrazine still can be adsorbed in a certain amount (0.034mmol/g). This implies that atrazine can occupy some sorption sites of WS750 that cannot be utilized by chlorpyrifos, such as these spaces between chlorpyrifoses as well as these pores that

chlorpyrifos cannot enter. Pseudo-first-order and pseudo-second-order models have been adopted to fit the kinetic sorption data

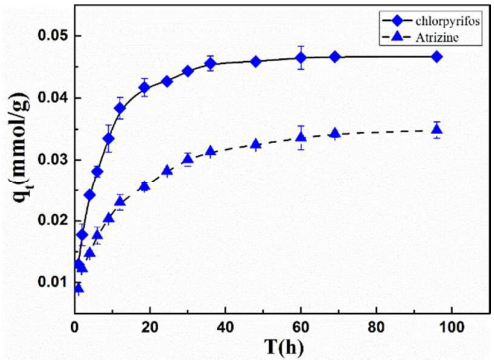

Fig.7 the kinetics sorption of the chlorpyrifos in the presence of atrazine (the full line with rhombus points) by WS750 and the kinetic sorption of atrazine in the presence of chlorpyrifos by WS750 (the dotted line with triangle points).

of atrazine by WS750 in the presence of chlorpyrifos and the kinetic sorption data of chlorpyrifos by WS750 in the presence of atrazine (Fig. S15 and Table. S4). The experimental sorption quantities are 0.047 mmol/g for chlorpyrifos and 0.034 mmol/g for atrazine. The sorption quantities from pseudo-first-order model are 0.0461 mmol/g for chlorpyrifos and 0.0305 mmol/g for atrazine, while the sorption quantities from pseudo-second-order model are 0.0488 mmol/g for chlorpyrifos and 0.0369 mmol/g for atrazine. Furthermore, the R^2 values from pseudo-first order model is 0.992 for chlorpyrifos and 0.907 for atrazine, while the R^2 values from pseudo-second -order model are 0.999 for chlorpyrifos and 0.998 for atrazine. Obviously, pseudo-second-order model can give a better description about the kinetic sorption of the coexisting atrazine and chlorpyrifos by WS750 than pseudo-first-order model.

For better understanding this experimental phenomenon, the pi-pi interaction between chlorpyrifos and WSmodel is calculated as well (please see Fig.S16), which is 23.68 kcal/mol, being larger than that between atrazine and WSmodel (22.70 kcal/mol) (please see Fig.2). Theoretical result accounts well why WS750 prefers to adsorb chlorpyrifos. In addition, the lipophilicity of chlorpyrifos (logP =4.7) and atrazine (logp=2.7) [44] may also play very important role in the sorption of the coexisting chlorpyrifos and atrazine by WS750 since the WS750 is of hydrophobic surface and prefers to adsorb more lipophilic chlorpyfifos than less lipophilic atrazine. Thus, pi-pi interaction and lipophilicity can both be used as indicators to assess the sorption quantities of the coexisting chlorpyrifos and atrazine by WS750 in competitive sorption.

The isotherm sorption of the coexisting chlorpyrifos and atrazine by WS750 is shown in Fig. 8. The concentrations of atrazine in the solution range from 0.35 mg L^{-1} (0.0016 mmol L^{-1}) to 0.73 mg L^{-1} (0.0034 mmol L^{-1}) and the concentrations of chlorpyrifos in the solution change from 0.56 mg L^{-1} (0.0016 mmol L^{-1}) to 1.19 mg L^{-1} (0.0034 mmol L^{-1}). According to Fig. 8, the sorption quantifies of chlorpyrifos and atrazine by WS750 all increase with the increased concentrations, and the sorption quantifies of chlorpyrifos are always larger than that of atrazine. Freundlich and Langmuir models have been adopted to investigate the isotherm sorption of the coexisting chlorpyrifos and atrazine by WS750. From Fig S17 and Table S5, the correlation coefficient R^2 values from Freundlich model are 0.998 for chlorpyrifos and 0.994 for atrazine, while that of R^2

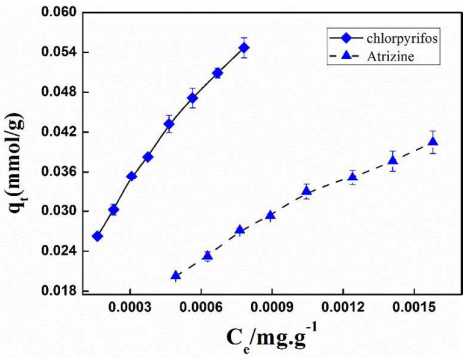

Fig.8 the isotherm sorption of the chlorpyrifos in the presence of atrazine (the full line with rhombus points) by WS750 and the isotherm sorption of atrazine in the presence of chlorpyrifos by WS750 (the dotted line with triangle points).

from Langmuir model are 0.989 for chlorpyrifos and 0.993 for atrazine. This means that Freundlich model is more suitable to describe the isotherm sorption of the coexisting chlorpyrifos and atrazine by WS750 than Langmuir model. This is different from that in separate isotherm sorption, in which Langmuir model is more suitable to describe the isotherm sorption of atrazine than Freundlich model. This maybe from that the presence of chlorpyrifos disturbs the sorption of atrazine on WS750 surface and in these pores of WS750, which makes that the sorption sites of WS750 are not uniform available for atrazine. This leads to that Freundich model is more suitable to describe the isotherm sorption of atrazine than Langmuir model in competitive sorption.

Furthermore, Sheindorf et al.[45] proposed a Freundlich-type multicomponent isotherm sorption equation (Sheindorf–Rebuhn–Sheintuch equation) to investigate isotherm sorption of multicomponent. From this isotherm equation, one can acquire the competitive coefficient between components in the multicomponent sorption.[46-47] Herein, Sheindorf–Rebuhn–Sheintuch equation is also used to acquire the competitive coefficients: $\alpha_{chlorpyrifos/atrazine}$ and $\alpha_{atrazine/chlorpyrifos}$ (Fig S18 and Table S6). The former means the influence of atrazine on the sorption of chlorpyrifos by WS750, while the latter means the influence of chlorpyrifos on the sorption of atrazine by WS750. According to Table S6, the R^2 values are 0.994 for $\alpha_{chlorpyrifos/atrazine}$ and 0.997 for $\alpha_{atrazine/chlorpyrifos}$, indicating that Sheindorf–Rebuhn–Sheintuch equation can describe the isotherm sorption of the coexisting chlorpyrifos and atrazine well. Furthermore, $\alpha_{chlorpyrifos/atrazine}$ is 0.213 and $\alpha_{atrazine/chlorpyrifos}$ is 1.287, implying that the influence of chlorpyrifos on the sorption of atrazine by WS750 is stronger than that of atrazine on the sorption of chlorpyrifos by WS750. This is consistant with the competitive sorption result of the coexisting chlorpyrifos and atrazine by WS750.

The recycle sorption performance of WS750 for the sorption of the coexisting chlorpyrifos and atrazine has been investigated as well. The concentration of atrazine is 0.69 mg L^{-1} (0.0032 mmol L^{-1}), and the concentration of chlorpyrifos is 1.12 mg L^{-1} (0.0032 mmol L^{-1}). The sorption ability of WS750 is regenerated by washing with

methanol. According to Fig. 9, the adsorption quantities of chalorpyrifos by WS750 are always larger than that of atrazaine by WS750 in three sorption experiments. Futhremore, the sorption quantities of both chlorpyrifos and atrazine decrease fast from the first sorption to

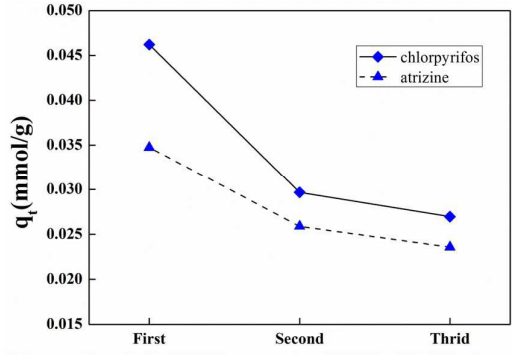

Fig. 9 Recycle experiments of WS750 for the sorption of the coexisting chlorpyrifos (the full line with rhombus points) and atrazine (the dotted line with triangle points) in solution.

the second sorption. This maybe from that the chlorpyrifos and atrazine adsorbed in these deep pores of WS750 can not be washed off by methanol. But, the sorption quantities of both chlorpyrifos and atrazine decrease a little from the second sorption to the third sorption, implying that most of chlorpyrifos and atrazine adsorbed in the second sorption experiment can be washed off by methanol. For the sorption of chlorpyrifos by WS750, the sorption quantities are 0.047 mmol/g in the first sorption and 0.027 mmol/g in the third sorption, in which just 58% sorption performance of WS750 for chlorpyrifos is recovered. For the sorption of atrazine by WS750, 70% sorption performance of WS750 for atrazine is recovered since the sorption quantities of atrazine are 0.034 mmol/g in the first sorption and 0.024 mmol/g in the third sorption. This is attributed to that the interaction between atrazine and WS750 is weaker than that between chlorpyrifos and WS750 (22.70 kcal/mol vs 23.68 kcal/mol). So, atrazine is more easily to be washed off by methanol than chlorpyrifos.

4 Conclusions

Detailed studies have been first time performed to investigate the sorption of atrazine and the competitive sorption of the coexisting atrazine and chlorpyrifos in solution by WS750. Based on these acquired results, some conclusions can be maken as following: (1) WS750 can effectively adsorb atrazine and the largest sorption

quantity is 37.0 mg/g. The sorption behavior follows pseudo-second-order and Langmuir models, while the driving force for sorption is pi-pi interaction. 72% sorption ability of WS750 for atrazine can be recovered by washing with methanol after the use of three times.

(2) In the separated sorption, WS750 has higher sorption quantity for atrazine (0.0556mmol/g) than that for chlorpyrifos (0.0537mmol/g), being due to that the molecular volume (268.8 Å3) of atrazine is smaller than that (350.8 Å3) of chlorpyrifos. Thus, molecular volume can be used as an indicator to assess the sorption quantities of chlorpyrifos and atrazine in separate sorption. It is very possible that molecular volume can also be used to evaluate the sorption quantities of same type of pollutants by biochar in separate sorption.

(3) In the competitive sorption, WS750 prefers to adsorb chlorpyrifos with respect to atrazine (0.0470mmol/g vs 0.034mmol/g), which is attributed to that chlorpyrifos has stronger pi-pi interaction with WS750 (23.68 kcal/mol) and larger lipophilicity (logP = 4.7) than that (22.70 kcal/mol, logP = 2.7) of atrazine. Thus, pi-pi interaction and lipophilicity can be used as indicators to assess the sorption quantities of the coexisting chlorpyrifos and atrazine in competitive sorption. It is very possible that pi-pi interaction and lipophilicity can also be used to evaluate the sorption quantities of same type of pollutants by biochar in competitive sorption.

(4) The isotherm sorption of the coexisting atrazine and chlorpyrifos by WS750 can be described well by sheindorf–Rebuhn–Sheintuch equation. For WS750, 58% sorption ability for chlorpyrifos and 70% sorption ability for atrazine can be recovered by washing with methanol after the use of three times, being due to that the interaction between atrazine and WS750 is weaker than that between chlorpyrifos and WS750 (22.70 kcal/mol vs 23.68 kcal/mol).

This work is helpful to understand the competitive sorption of bi-pollutant in waste water.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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

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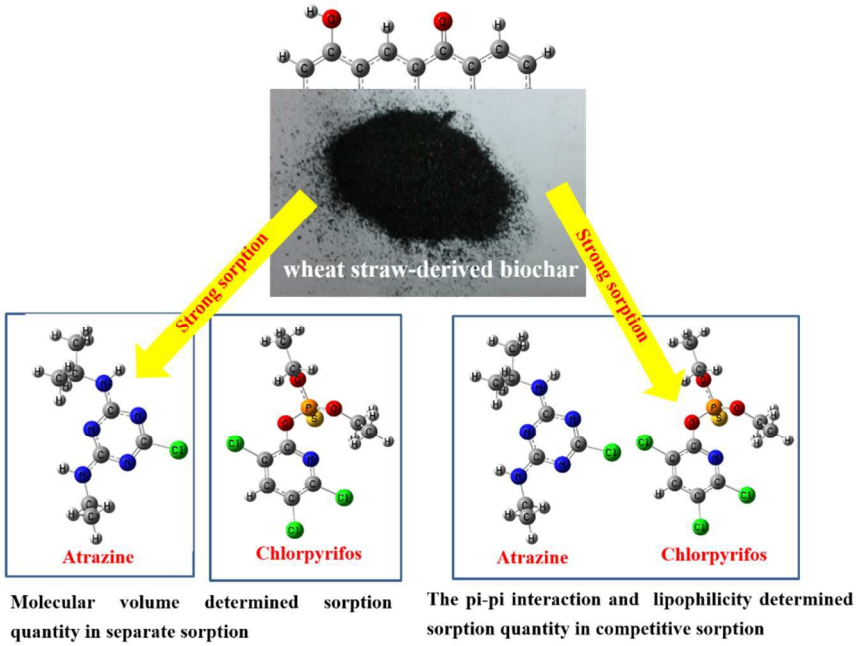

In separate sorption, wheat straw-derived biochar (WS750) has higher sorption quantity for atrazine than chlorpyrifos since the molecular volume (268.8 $Å^3$) of atrazine is smaller than that (350.8 $Å^3$) of chlorpyrifos. In competitive sorption, WS750 prefers to adsorb chlorpyrifos with respect to atrazine, being due to that chlorpyrifos has stronger pi-pi interaction with WS750 (23.68 kcal/mol) and larger lipophilicity (logP = 4.7) than that (22.70 kcal/mol, logP = 2.7) of atrazine.