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Remove of Chlorpyrifos from Waste Water by Wheat Straw-Derived Biochar Synthesized through Oxygen-Limited Method

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Systematic studies have been first time performed to investigate the pyrolysis behavior of wheat straw and the adsorption mechanism of chlorpyrifos by wheat straw-derived biochar. FTIR and elemental analysis results indicate that aromatic and hydrophobic substances are produced during the pyrolysis progress of wheat straw. BET results suggest that the pyrolysis temperature of wheat straw should be above 450 °C if one will acquire the biochar with surface area above 60.0 $m^2 g^{-1}$. The adsorption experiments show that wheat straw-derived biochar at 750 °C (WS750) can effectively adsorb chlorpyrifos and the largest adsorption quantity is 16 mg/g. The driving force for chlorpyrifos adsorption by WS750 is most likely attributed to the *л…л* stack between the aromatic ring of chlorpyrifos and these aromatic areas on WS750 surface. The adsorption behaviors follow the pseudo-second kinetic and Freundlich models. Recycle experiments show that the adsorption ability of WS750 can be recovered by washing with methanol. The present work shows that wheat straw-derived biochar can work as a high effective and low cost adsorbent to remove chlorpyrifos from waste water.

1. Introduction

China is a large agricultural country since it has nearly the 1/4 of the world population to support. For making sure the high yield of crops, such as wheat and rice, pesticides have been widely used to kill pests. As a broad spectrum organophosphate pesticide, the toxicity of chlorpyrifos is lower than that of other organophosphate pesticides, such as meshamidophos and ammonium phosphate.[1] So, chlorpyrifos has been used to replace these highly toxic organophosphate pesticides for killing agricultural pests. However, it has reported that chlorpyrifos can transfer into river from farmland, which is toxic for some species in water, e.g. frog and fish.[1] Some methods have been developed to remove chlorpyrifos from water. Chishti et al used microorganisms to degrade chlorpyrifos in water.[2] Weston et al suggested that enzymes could be applied to evaluate and reduce the toxicity of chlorpyrifos in water.[3] TiO_2 was used to photodegrade chlorpyrifos in water by Kanmoni et al.[4] Adsorption is the commonly used method to remove these contaminants from water since of its simplicity and low cost.[5] Presently, most of researches focus on the adsorption and desorption of chlorpyrifos to soil.[6] Reports using adsorbents to remove chlorpyrifos from water are rare. Zhao et al[7] has found that the residual of drinking water treatment material can effectively adsorb chlorpyrifos in water with respect to paddy soil, which contains iron, aluminium hydroxide minerals and humic materials. And, the largest adsorption quantity is about 1.2mg/g.[7] It is still necessary to develop low cost and high effective adsorbents for removing chlorpyrifos from waste water.

As a large agricultural country, the wheat yield in China is very high,[8] which leads to a large number wheat straw. The traditional way of treating wheat straw is to directly burn them in the field, which has resulted in serious air contamination.[9] For reducing environmental pollution and waste recycling, many methods have been developed to reuse wheat straw, in which using wheat straw to produce biochar is the promising one since biochar can be applied to soil remediation, carbon dioxide fixation and adsorbent due to its large surface area and high microporosity.[10] Usually, wheat straw is converted into biochar in anoxic condition under high temperatuer.[11] However, the cost is high since inert gas, such as nitrogen, is needed for keeping a anoxic condition during carbonization process. In addition, the requirement for gas tightness of muffle furnace is high as well. For lowing the cost and simplifying the carbonization procedure, oxygen-limited method has been developed to synthesize biochar, in which oxygen availability was restricted by using a cover to close feedback in crucible.[12] Junna et al has prepared biochar with oxygen-limited method by using aluminium foil to wrap wheat straw during heating process.[13] Using cover to close wheat straw in crucible may be a better method to keep an oxygen-limited condition than that of using aluminium foil since the former is easier to use in a large-scale, can withstand higher temperatures and has a

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better gas tightness. Furthermore, surface area is a very crucial parameter for evaluating the adsorption ability of biochar. So far, the relationship between surface area and pyrolysis temperature of wheat straw derived biochar has not been investigated.

Currently, the studies on wheat straw derived biochar focus on using them to remediate the contaminated soil, such as to immobilize chlorobenzenes in soil,[14] to replace peat in soilless substrates,[15] and to adsorb cadmium cations in soil.[16] Report using wheat straw derived biochar to remove chlorpyrifos from water has not been found.

Herein, a detailed research has been first time performed to investigate the relationship between surface area and pyrolysis temperature of wheat straw derived biochar synthesized through oxygen-limited method, in which oxygen availability is restricted by using a cover to close wheat straw in crucible and the temperature varies from 250 °C to 750 °C. Then, these as-prepared biochar are used to adsorb chlorpyrifos for evaluating their adsorption ability. The obtained results show that wheat straw derived biochar can effectively remove chlorpyrifos from water. This work is helpful to promote the application of wheat straw derived biochar to purify waste water.

2. Experimental Section

2.1. Preparation of biochar

Wheat straw was first washed to remove mud and other impurities attached on its surface, followed by drying at 80°C for overnight. Then, the dried wheat straw was crushed into powder through a disintegrator and subsequent passed through a 20 mesh sieve. After that, the obtained wheat straw powder was filled to the full crucible and the volume of the crucible was 100 ml. Whereafter, the crucible was closed with cover and heated in furnace at 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C for two hours, respectively. The heating rate was 10°C/min. These acquired biochar samples were first washed with 1 mol/L HCl to remove soluble minerals, and followed by the washing with deionized water to neutral state. These as-prepared samples were named as WS250, WS350, WS450, WS550, WS650 and WS750, respectively.

2.2. Characterization of samples

The thermal stability of wheat straw was characterized by thermogravimetric analysis (Netzsch STA 449 F1 Jupiter, Germany). The H/C ratio in WS750 was determined by elemental analysis on the elemental analyzer (vario EL II, Elementar, Germany). The Fourier transform infrared spectrum spectra of WS250, WS350, WS450, WS550, WS650 and WS750 samples were acquired using Nexus 870 FT-IR instrument (USA). The surface areas of WS250, WS350, WS450, WS550, WS650 and WS750 samples were determined with HD88, ASAP2020 micropore analyzer (USA). The morphology of WS750 was investigated with JEM-2100 electron microscope (Japan). Zeta potentials of WS750 at different pH were performed using the Zetasizer Nano ZS (UK).

The chlorpyrifos concentration was determined at a wavelength 300 nm using High Performance Liquid Chromatography (HPLC, Waters e2696, USA) with a UV detector (Waters 2489) and a column (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°C. The injected sample volume was 100 μL and the retention time was 3.9 min.

2.3. Adsorption experiments

2.3.1. Adsorption experiments of chlorpyrifos by WS250, WS350, WS450, WS550, WS650 and WS750 samples

The solubility of chlorpyrifos in water is just 1.2mg/L. So, a stock solution of chlorpyrifos (2.5g/L) was first prepared by dissolving chlorpyrifos in methanol. The stock solution was diluted into a specific concentration with 0.005 mol/L $CaCl_2$ solution for the adsorption test.

2.5mg biochar sample was weighted and put into an EPA bottle and the bottle cap has teflon gasket. EPA bottle was purchased from Shanghai ANPEI Instrument Co. Ltd, China. Then, 0.80mg/L chlorpyrifos was filled into the EPA bottle, followed by rotation for 48 hours with the rotation rate (70 r/min) at room temperature under dark conditions. Three parallel experiments were performed for each biochar sample. After adsorption experiments were finished, the supernatants in these EPA bottles were taken for determining the adsorption effect with HPLC method.

2.3.2. Adsorption isotherms of chlorpyrifos by WS750

A series of chlorpyrifos solutions with concentration ranged from 0.40 mg/L to 1.2 mg/L were prepared for investigating the adsorption isotherm of chlorpyrifos by WS750. The procedure of chlorpyrifos adsorption by WS750 was same as that mentioned in 2.3.1 section.

2.3.3. Adsorption kinetics of chlorpyrifos by WS750

The procedure of chlorpyrifos adsorption by WS750 was same as that mentioned in 2.3.1 section. The concentration of chlorpyrifos was 0.80mg/L. The samples were collected at time intervals of 0.5, 1, 2, 4, 6, 8, 10, 12, 24, 36, 48, 60 and 72 hours of rotation.

2.3.4. Adsorption experiment of chlorpyrifos by the inorganic component in WS750

5.0g WS750 sample was put into crucible and was heated at 800 °C for two hours without cover. The ash in the bottom of crucible was collected for investigating its ability to adsorb chlorpyrifos. The adsorption procedure was same as that mentioned in 2.3.1 section.

2.3.5. The effect of $CaCl_2$ concentration on the adsorption of chlorpyrifos by WS750

The effect of $CaCl_2$ concentration on the adsorption of chlorpyrifos by WS750 was also investigated. The concentrations of $CaCl_2$ ranged from 0.005mol/L, 0.010 mol/L, 0.050 mol/L to 0.100 mol/L in the diluted chlorpyrifos solution. The concentration of chlorpyrifos is

0.80 mg/L. The adsorption procedure was same as that mentioned in 2.3.1 section.

2.3.6. The pH effect on the adsorption of chlorpyrifos by WS750

The effect of pH on the adsorption of chlorpyrifos by WS750 was investigated as well. The pH of the diluted chlorpyrifos solution was adjusted to 3.05, 4.15, 5.23, 6.12 and 7.06, respectively. The concentration of chlorpyrifos is 0.80 mg/L. The adsorption procedure was same as that mentioned in 2.3.1 section. We did not consider the adsorption of chlorpyrifos by WS750 in basic condition since chlorpyrifos would be decomposed in basic condition.[1, 7]

2.3.7. Recycle experiment for adsorption of chlorpyrifos by WS750

The adsorption procedure was same as that mentioned in 2.3.1 section. Three parallel experiments were performed for the adsorption of chlorpyrifos by WS750. After the adsorption experiment was finished, WS750 was collected and washed with methanol, then followed by the reuse of the collected WS750 to adsorb chlorpyrifos. This procedure was repeated three times.

3. Results and discussion

A detailed analysis has been first performed to investigate the surface areas of these as-prepared biochar samples. According to Table 1, the pore volumes and pore diameters of WS250 and WS350 are not detected by micropore analyzer, suggesting that pore has not been formed in these two samples. Accordingly, the surface areas of WS250 and WS350 are just 0.114 $m^2 g^{-1}$ and 0.432 $m^2 g^{-1}$, respectively. Then, the pore volumes and pore diameters of WS450, WS550, WS650 and WS750 become larger with the increased pyrolysis temperature, and surface area increases from 63.5 $m^2 g^{-1}$ of WS450 to 467 $m^2 g^{-1}$ of WS750. One obvious increase of surface area can be found according to Table 1: it is between 350 °C and 450 °C, in which the surface area increases from 0.432 $m^2 g^{-1}$ to 63.5 $m^2 g^{-1}$. This implies that a pyrolysis temperature of 450 °C at least is needed for using wheat straw to produce biochar with oxygen-limited method since a significant surface area can just be acquired when pyrolysis temperature is above 450 °C. As far as we know, this is first time to make a clear description about the relationship between the surface area and the pyrolysis temperature of wheat straw-derived biochar, which is helpful for researchers to choose an appropriate pyrolysis temperature to produce wheat straw-derived biochar with large surface area.

Table.1 BET-N_2 Surface Area, Pore volume, Pore diameter, Ash Content and Yield of these as-prepared WS250-WS750 samples.

Biochar	T(°C)	BET ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)	Ash (%)	Yield (%)
WS250	250	0.114	/	/	1.9	67.4
WS350	350	0.432	/	/	5.7	36.9
WS450	450	63.5	0.01	1.83	8.5	29.9
WS550	550	303	0.16	2.13	9.7	26.1
WS650	650	336	0.18	2.14	11	24.9
WS750	750	467	0.26	2.19	12	21.5

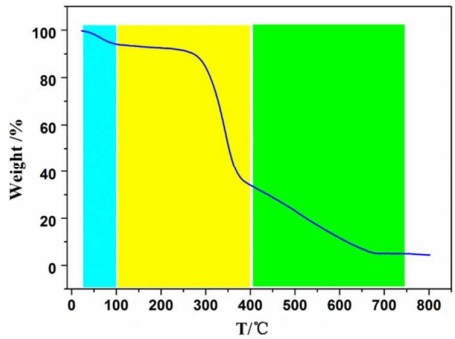


Fig.1 Thermogravimetric analysis of wheat straw.

For deep understanding the relationship between surface area and pyrolysis temperature of wheat straw-derived biochar, a thermogravimetric analysis (TGA) has been performed to investigate the pyrolysis behavior of wheat straw. It has reported that the components of wheat straw are mainly lignin, cellulose and hemicellulose,[17] in which cellulose and hemicellulose are decomposed from 350 °C to 400 °C, while lignin will be decomposed at a higher temperature than 400 °C.[17-18] According to Fig.1, three weight loss intervals are found from the TGA curve of wheat straw. The first one ranges from 25 °C to 100 °C, which is from the loss of the adsorbed water in wheat straw. The second one starts from 100 °C to 400 °C, being due to the thermal decomposition of cellulose and hemicellulose.[17-18] The third one ranges from 400°C to 700 °C, being attributed to the thermal decomposition of lignin.[17-18] By comparing Table.1 and Fig.1, one can deduce that the thermal decomposition of cellulose and hemicellulose will result in the formation of pore, and is most likely responsible for the abrupt increase of surface areas from WS350 to WS450. Furthermore, the surface areas from WS450 to WS750 continue to increase with the increase of pyrolysis temperature, which may be from the contribution of the pyrolysis of lignin at the higher temperature than 450 °C. So, the TGA result of wheat straw accounts well for the observed surface area results of wheat straw-derived biochar samples.

FTIR analysis has been further applied to investigate the pyrolysis process of wheat straw (Fig. S1). The broad peak around 3412 cm^{-1} and the peak at 2920 cm^{-1} are from the vibrations of O-H and aliphatic C-H_2 groups, respectively, while the peak at 1573 cm^{-1} is assigned to the vibration of the aromatic C=C bond.[19] According to Fig. S1, the peaks of 3412 cm^{-1} and 2920 cm^{-1} gradually disappear, while the peak of 1573 cm^{-1} gradually appears. This suggests that pyrolysis of wheat straw with the increased pyrolysis temperature will result in the formation of the aromatic and hydrophobic substances. In addition, the peak around 1100 cm^{-1} in the FTIR curve

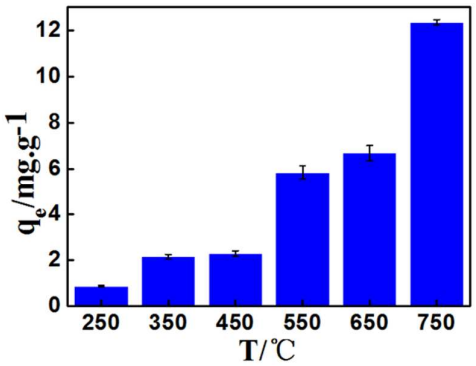


Fig.2 Comparison of chlorpyrifos adsorption by WS250-WS750 samples. The concentration of chlorpyrifos is 0.80 mg/L.

of WS750 is from the contribution of C-O and C-O-C groups, [19] implying that there are still some oxygen-containing functional groups on the surface of WS750 sample.

Chlorpyrifos is a broad spectrum organophosphate pesticide, which is toxic for some species in water, e.g. frog and fish.[1] According to our knowledge, wheat straw-derived biochar has not been used to adsorb chlorpyrifos from waste water. Herein, we first investigate the solubility of chlorpyrifos in water since it does not easy dissolve in water. According to Fig. S2, chlorpyrifos can dissolve well in water when the concentration is smaller than 1.2 mg/L. So, the concentrations of chlorpyrifos in this work are all smaller than 1.2 mg/L for avoiding the possible self-aggregation of chlorpyrifos. Then, we compare the adsorption ability of WS250-WS750 samples for chlorpyrifos. Based on Fig.2, WS750 has highest adsorption ability for chlorpyrifos in all samples (about 12 mg/g), being due to that the aromatic and hydrophobic degree of WS750 is highest among all samples and chlorpyrifos has an aromatic ring as well. Thus, WS750 is chosen as model compound of wheat straw-derived biochar and further studies have been performed to investigate the adsorption mechanism of chlorpyrifos by WS750.

Further characterizations about WS750 have first been done. According to the TEM image (Fig.S3), the structure of WS750 is loose and there are many pores on its surface, which is consistent with the surface area result of WS750 (Table.1). The ratio of H/C is usually used to characterize the aromatization degree of biochar sample. For example, the ratios of H/C between 0.13 and 0.37 all suggest that the biochar samples have highly aromatic structure.[19] The H/C ratio of WS750 is 0.25, supporting that the aromatization degree of WS750 is high, which is line with the FTIR analysis result of WS750. The inorganic constituents in WS750 is analysed through EDS method as well. Based on Fig. S4, the contents of O (55%, weight percentage) and Si (34%) are significant higher than the rest elements, such as Na (0.08%), Al(0.38%), K(1.1%), Ca (3.6%), S(1.4%) and P(1.1%), suggesting that the

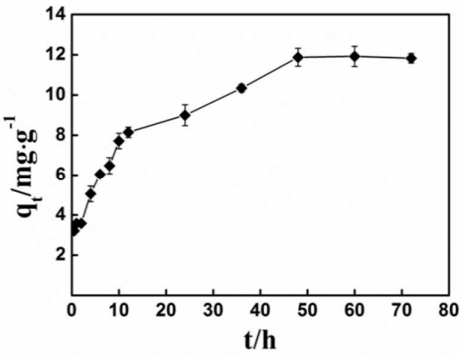


Fig.3 The chlorpyrifos adsorption by WS750 at 0.5, 1, 2, 4, 6, 8, 10, 12, 24, 36, 48, 60 and 72 hours, respectively. The concentration of chlorpyrifos is 0.80 mg/L.

inorganic constituent in WS750 is mainly SiO_2.

The adsorption kinetics of chlorpyrifos by WS750 has been done by detecting the concentration of chlorpyrifos taken at 0.5, 1, 2, 4, 6, 8, 10, 12, 24, 36, 48, 60 and 72 hours, respectively. From Fig. 3, the adsorption of chlorpyrifos by WS750 includes two adsorption periods: fast adsorption and slow adsorption. Fast adsorption period is from 0 hour to 12 hours, and nearly 70% chlorpyrifos is adsorbed in this period. Slow adsorption period ranges from the 12 hours to 48 hours and the rest 30% chlorpyrifos is adsorbed. After 48 hours, the adsorption equilibrium arrives. Pseudo-first-order and pseudo-second-order models have been used to analyse the kinetic adsorption of chlorpyrifos by WS750 (Fig. S5 and Table. S1).[20] The experimental adsorption quantity of chlorpyrifos is 12mg/g, while the adsorption quantity of chlorpyrifos from pseudo-first-order model and pseudo-second-order model are 11.080±0.560mg/g and 12.195±0.593mg/g, respectively. Furthermore, the R2 from pseudo-second-order model is 0.991, while the R2 from pseudo-first-order model is 0.841. All of this suggest that the adsorption of chlorpyrifos by WS750 follows the pseudo-second-order kinetic. This implies that the adsorption sites on WS750 are not homogeneous, which are consistent with FTIR and TEM results. According to FTIR and BET results (Fig. S1 and Table.1), WS750 has aromatic surface and cavity with diameter larger than 2.19 nm. Fast adsorption is most likely from the adsorption of chlorpyrifos on the aromatic areas of WS750 surface and the mouth of the cavity in WS750. And the slow adsorption is possible from the transfer of chlorpyrifos from the mouth to the inside of the cavity.

The adsorption isotherm of chlorpyrifos by WS750 has been investigated as well. According to Fig. 4, the adsorption quantify of chlorpyrifos by WS750 increases with the increased concentration of chlorpyrifos, and the largest adsorption quantify is around 16 mg/g. Freundlich method is usually used to describe the adsorption behavior of biochar.[21] From Fig S6 and Table S2, the correlation coefficient R^2 is 0.968, implying that Freundlich method can describe well the adsorption

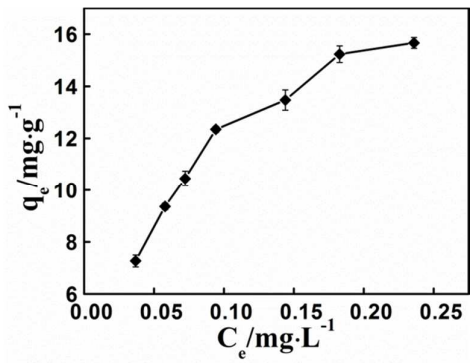


Fig.4 The adsorption isotherm of chlorpyrifos by WS750. The concentration of chlorpyrifos ranges from 0.40 mg/L to 1.2 mg/L.

behavior of chlorpyrifos by WS750. The K and 1/n values from Freundlich fitting results are 30.265±4.852 and 0.413±0.0187, respectively, implying that WS750 has strong affinity for chlorpyrifos. There is an aromatic ring in chlorpyrifos, and some areas on WS750 surface are aromatic. Thus, the affinity between chlorpyrifos and WS750 maybe from the л…л interaction between the aromatic ring of chlorpyrifos and these aromatic areas on WS750 surface. [22-25]

There is inorganic component in WS750 and EDS result has confirmed that the inorganic component is mainly SiO_2. An adsorption experiment has been performed to clarifying the role of the inorganic component in the adsorption of chlorpyrifos by WS750. The acquired result shows that the inorganic component in WS750 does not adsorb chlorpyrifos.

$CaCl_2$ has been added in the diluted chlorpyrifos solution for keeping a constant ionic strength.[7] Series adsorption experiments have been done to investigate the influence of $CaCl_2$ concentration on the adsorption of chlorpyrifos by WS750. According to Fig. 5, the adsorption quantity of chlorpyrifos by WS750 decreases with the increased $CaCl_2$ concentration. This may be due to that these increased ions (Ca^{2+} and Cl^-) can occupy the adsorption sites on the surface of WS750 through ion…л interaction, [7, 24-25] which leads to the decrease of chlorpyrifos

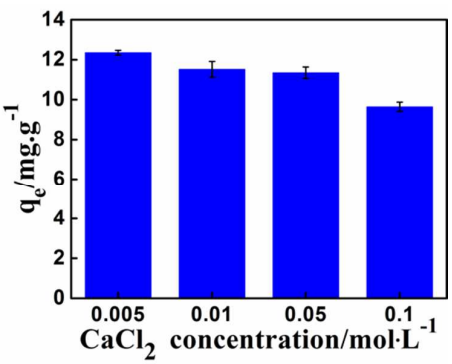


Fig.5 The influence of $CaCl_2$ concentration on the adsorption of chlorpyrifos by WS750. The concentration of chlorpyrifos is 0.80 mg/L.

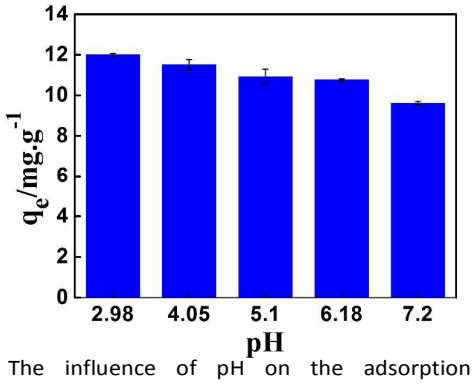


Fig.6 The influence of pH on the adsorption of chlorpyrifos by WS750. The concentration of chlorpyrifos is 0.80 mg/L.

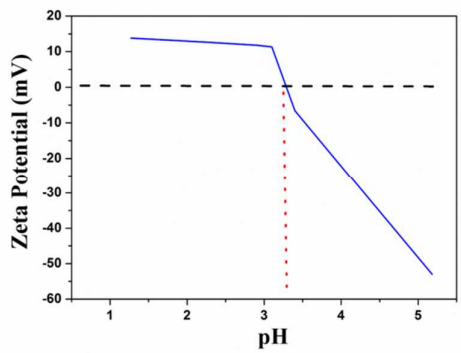
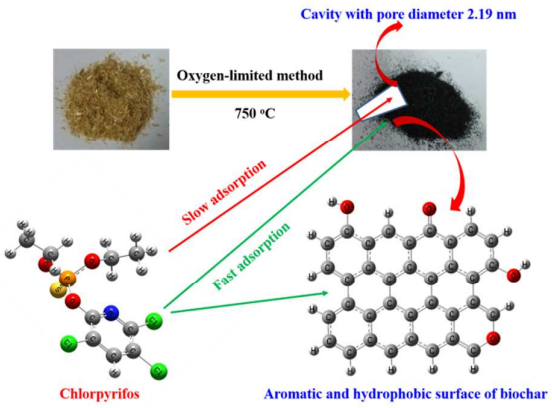


Fig.7 The surface charge of WS750 at different pH values.

adsorption.

A detailed adsorption experiments have also been performed to investigate the influence of pH on the adsorption of chlorpyrifos by WS750. According to Fig. 6, the adsorption quantity decrease with the increase of pH. For better understanding the experimental observation, the surface charge of WS750 at different pH has been investigated as well. The surface charge of WS750 at basic situation is not investigated since chlorpyrifos will hydrolysed at basic condition. Based on Fig. 7, the surface charges of WS750 change from positive to negative with the increase of pH from 1.27 to 5.18. The zero point charge of WS750 surface is around pH3.30. The change of charge on WS750 surface at different pH is most likely due to the protonation/deprotonation of oxygen-containing functional groups on WS750 surface. From Fig. S1, the peak around 1100 cm^{-1} supports the existence of C-O and C-O-C groups.[19] In most of case, cation is most likely to interact with aromatic ring than anion.[26-27] So, it is easily to explain why WS750 with positive surface has a stronger adsorption for chlorpyrifos than that with negative surface. In addition, there are O atoms in chlorpyrifos. This means that the possible hydrogen bonding interaction between the proton on WS750 surface and O atoms in chlorpyrifos may also exist, [23] which will further increase the adsorption of chlorpyrifos by WS750 under low pH condition.

A possible adsorption mechanism has been proposed to explain the adsorption behavior of chlorpyrifos by WS750. FTIR, elemental analysis and BET results show that some areas on WS750 surface are aromatic and hydrophobic, while the diameter of cavity in the inside of WS750 is about 2.19 nm. There is an aromatic ring in chlorpyrifos and its size is less than 2.19 nm. Based on the fitting results from Freundlich and pseudo-second-order models, WS750 has strong attraction for chlorpyrifos and the adsorption behavior include two periods: fast adsorption and slow adsorption. From Scheme.1,



Scheme.1 The possible adsorption mechanism of chlorpyrifos by wheat straw derived biochar synthesized through oxygen-limited method.

the *л*…*л* interaction between the aromatic ring of chlorpyrifos and the aromatic areas on WS750 surface may be responsible for the effective adsorption of chlorpyrifos by WS750.[22-25] Fast adsorption is most likely from the adsorption of chlorpyrifos on the aromatic areas on WS750 surface and the mouth of the cavity in WS750, while the slow adsorption is possible from the transfer of chlorpyrifos from the mouth to inside of the cavity.

The recycle adsorption experiments of WS750 have also been performed to explore the possibility of using WS750 as adsorbent to clean waste water in real situation. The adsorption ability of WS750 is recovered by washing with methanol. According to Fig. S7, the adsorption quantity of WS750 decrease to 7.5 mg/g in the second time from the 12 mg/g in the first time, suggesting that washing can just recover the 63% adsorption ability of WS750. Interestingly, the adsorption ability of WS750 in the third time is nearly same as that in the second time. According to Fig. 3 and Scheme.1, 70% chlorpyrifos is adsorbed by WS750 in the fast adsorption period. So, the chlorpyrifos adsorbed on WS750 surface is easily to be washed by methanol, but the disadsorption of chlorpyrifos in the cavity is not easily. However, the adsorption quantity (7.5mg/g) is still higher than the reported one (1.2mg/g),[7] and the recovery method is very simple. So, it is feasible to use WS750 as adsorbent for purifying waste water.

4. Conclusions

In summary, systematic studies have been performed to investigate the pyrolysis behavior of wheat straw and the adsorption mechanism of chlorpyrifos by wheat straw-derived biochar. BET results suggest that the pyrolysis temperature of using wheat straw to produce biochar should be above 450 ^{o}C. FTIR and elemental analysis support that the pyrolysis of wheat straw will lead to the appearance of the aromatic and hydrophobic substances. The adsorption experiments show that WS750 can effectively adsorb chlorpyrifos and the largest adsorption quantity is 16 mg/g. The driving force for chlorpyrifos adsorption by WS750 is mainly from the *л*…*л* interaction between the aromatic ring of chlorpyrifos and the aromatic areas on the surface of WS750. Recycle experiments show that the adsorption ability of WS750 can be recovered by washing with methanol. The present work will be helpful to promote the application of wheat straw-derived biochar to the purification of 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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