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Controlling Pesticide Loss by Natural Porous Micro/Nano Composites: Straw Ash-Based Biochar and Biosilica

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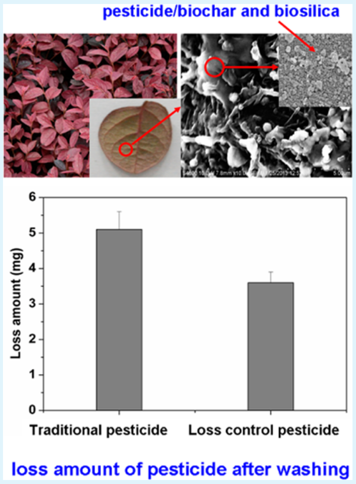
ABSTRACT: Pesticide sprayed onto plant leaves tends to discharge into the environment through rainwater washing, leaching, and volatilization, resulting in severe pollution to soil, water, and air. Here, to control pesticide loss, we developed a loss-control pesticide (LCP) by adding straw ash-based biochar and biosilica (BCS) to traditional pesticide. BCS possesses a porous micro/nano structure and thus can adsorb a large amount of pesticide molecules to form pesticide−BCS complexes that tend to be retained by the rough surface of plant leaves, displaying a high adhesion performance on the leaves; therefore, the pesticide loss decreases, sufficient pesticide for the plant is supplied, and the pollution risk of the pesticide can be substantially lowered.



KEYWORDS: *loss-control pesticide, biochar and biosilica, chlorpyrifos, adhesion*

1. INTRODUCTION

Pesticide has played a key role in modern agriculture, showing substantial agronomic and economic benefits. However, it also poses an environmental risk resulting from its loss resulting from drift-off, runoff, and volatilization from plant leaves because of both rainy and windy weather as well as leaching in soil, which can cause soil, groundwater, and air contamination. To compensate for the loss and to ensure an adequate durable period, excessive amounts of pesticides are used, and the risk of environmental contamination is also increased.[1] Such situations may get worse in a rainy season or area. Therefore, an advanced pesticide with a low loss demands to be developed.

Nowadays, a great many types of slow-release pesticide formulations have been developed through encapsulating[2] in the form of microcapsules,[3] tablets,[4,5] and so forth using polymers, clays, and so on. Although they can effectively prolong the durable period, the released unused pesticide tends to discharge to the environment through washing, leaching, and volatilization, resulting in severe environmental pollution and a waste of manpower and energy. Therefore, controlling pesticide loss is believed to be a fundamental and promising approach to decrease the environmental exposure to pesticide. To reduce the possibility of environmental pollution and save manpower and energy, it is important to develop a new kind of pesticide with properties of high adhesion capacity on the leaf surface, low loss amount, long efficacy duration, low dosage, fewer use times, and high safety compared with traditional pesticide. In this article, we describe a new kind of formulation of pesticide named loss-control pesticide (LCP) by adding appropriate amounts of straw ash-based biochar and biosilica (BCS), as the loss-control agent (LCA), to traditional pesticide.

Because of its renewable property, biomass is gaining increasing attention as the fuel for generating electricity through combustion all over the world, especially in developing countries. At present, around 12% of the global energy is generated by the combustion of biomass fuels, and around 35% of the energy comes from biomass in developing countries. Therein, about 30−40% of the biomass originates from straw. In China, more than 0.7 billion tons of straw are produced annually, wherein approximately 10 million tons of straw are used for generating electricity through combustion, producing at least 500 000 tons of straw ash.[6−8] With a fast developing economy, more biomass, especially straw, will be burned for electricity, producing more straw ash. However, a lack of recycling technology makes straw ash hard to reuse, resulting in the occupation of land and environmental pollution.[9] Hence, it

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is necessary to develop an effective technology for straw ash utilization. Straw ash mainly consists of BCS, which possesses a micro/nano structure with high porosity, large specific surface area, and negative surface charge, exhibiting a high adsorption capacity and stability, especially for organic matter.[10] Additionally, BCS is favorable to plant growth.[11] Consequently, BCS was selected here as a LCA for pesticide because BCS could adsorb a great amount of pesticides into the micro/nano pores, forming a BCS−pesticide complex. This complex tended to be retained on the leaf surface because of the rough morphology of the leaf surface and thus the loss of pesticide could be controlled.

Chlorpyrifos (CPF) (*O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)-phosphorothioate), a broadspectrum organophosphorus insecticide, was selected as the model pesticide here because of its wide application for controlling rice thrips, gall midge, planthoppers, rice leafhopper, termites, and so on as well as because of the potential adverse impact on ecosystems or human health.[12−15] CPF tends to leach into groundwater, get into the atmosphere through volatilization, and travel long distances, resulting in a huge risk for the environment. The objective of this work is to develop a new formulation of pesticide, named loss-control formulation of chlorpyrifos (LCC), using BCS and to investigate the adhesion performance of LCC on plant leaves and the migration performance through soil leaching and volatilization in comparison with CPF alone. It was shown that BCS could significantly improve the adhesion ability of CPF. This work may provide not only a promising method to control pesticide loss and reduce the pollution risk to the environment but also a potential utilization technology for the straw ash generated from biomass power plants. This loss-control technique can be suitable for pesticides applied through spraying only.

2. EXPERIMENTAL SECTION

2.1. Materials. Straw ash-based biochar and biosilica, with approximately 60% carbon and 35% SiO_2 and an average particle size of 10 μm, was provided by Kaidi Electric Power Co., Ltd. (Wuhan, China). CPF with a purity of 99% was provided by Jinghong Chemical Co. Ltd. (Jiangsu, China). Other chemicals were of analytical reagent grade and were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Deionized water was used throughout this work. Red Flowered Loropetalum leaves, each with area of approximately 2 cm^2, were taken from the campus of Anhui Agricultural University.

2.2. LCC Emulsion Preparation. CPF (3.84 g) was dissolved in 15 mL of petroleum ether, 1 mL of tween 80 was added to the system, and additional petroleum ether was added, making the volume of solution 20 mL. Afterward, 1 mL of the resulting solution was added to 35 mL of deionized water and then additional deionized water was added, making the volume of system 40 mL and obtaining the CPF emulsion with a concentration of 4.8 g/L. Without the loss-control agent, this CPF emulsion was used as the control and designated as LCC0. Next, 0.2, 0.4, 0.6, 0.8, and 1.0 g of BCS was added to the CPF emulsion, and the resulting suspensions samples were designated as LCC1, LCC2, LCC3, LCC4, and LCC5, respectively.

2.3. Washing Performance Investigation. LCC emulsion (100 mL) was put into a beaker. A leaf was placed into the beaker and then removed after soaking for about 5 s to reach the absorption equilibrium. In one case, the leaf was immediately transferred to 100 mL of distilled water and washed steadily for 10 s, and in another case, after air-drying for 10 min, it was transferred to 100 mL of distilled water and washed steadily for 10 s. Herein, the former approach was designated as wet washing and the latter approach was designated as dry washing. For either of these two approaches, the resulting leaf was put into 5 mL of petroleum ether and shaken for 5 min to extract the remaining CPF from the leaf surface, and the concentration of CPF in the petroleum ether was determined thereafter.

2.4. Leaching Behavior Investigation. Two grams of soil (150−200 mesh) was put into a centrifuge tube (2.5 mL). A hole (diameter of 2 mm) was opened at the bottom of the tube with a little cotton below the soil layer to prevent the soil from leaching out. Two milliliters of LCC emulsion was added dropwise to the top of the soil layer. After 1 h, the leachate was collected and extracted with 5 mL of petroleum ether, from which the concentration of CPF was measured afterward.

2.5. Volatilization Performance of CPF from Leaf Surface. A leaf was transferred into a petri dish after being soaked in 100 mL of LCC emulsion for about 5 s. The petri dish was put into a fume hood at 20 °C under air flow of 3.6, 4.8, and 6.0 km/h. After volatilization for 30 min, the leaf was transferred into 5 mL of petroleum ether and shaken for 5 min to extract the remaining CPF from the leaf surface, from which the concentration of CPF was determined thereafter.

2.6. Volatilization Performance of CPF Emulsion. A petri dish with 5 mL of LCC emulsion was put into a fume hood at a required temperature (15, 20, 25, 30, 35, and 40 °C) under a required air flow (3.6, 4.8, and 6.0 km/h). After volatilization for 30 min, 5 mL of petroleum ether was added to the petri dish and shaken for 5 min to extract the remaining CPF, from which the concentration of CPF was determined thereafter.

2.7. Characterization. The morphology of BCS, leaf, and BCS-CPF-leaf were observed on a scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDX) (Sirion 200, FEI Co., USA). The structure and interaction were analyzed using a TTR-III X-ray diffractometer (XRD) (Rigaku Co., Japan) and Fourier transform infrared (FTIR) spectrometer (Bruker Co., Germany). The concentration of CPF in the petroleum ether was measured using a UV−vis spectrophotometer (UV 2550, Shimadzu Co., Japan) at a wavelength of 293 nm.[16]

3. RESULTS AND DISCUSSION

3.1. Morphology and Microstructure Modification Investigation. BCS consists of mainly micro/nano (50−200 nm) carbon and silica particles. It has a porous nanostructure with a pore scale ranging from 1 to 200 nm (inset of Figures 1 and 2h) and negative surface charges, resulting in a high specific surface area (50−150 m^2/g) and surface activity. Consequently, it can be potentially used as an ideal adsorbent to adsorb CPF molecules into the pores and onto the surface, forming BCS−CPF complex micro/nano particles (actually the LCC), as shown in Figure 2g. Naturally, the leaf surface illustrated a 3D network morphology with a pore size of 10−100 μm (Figure 2b,c), which could provide sufficient space to house BCS−CPF

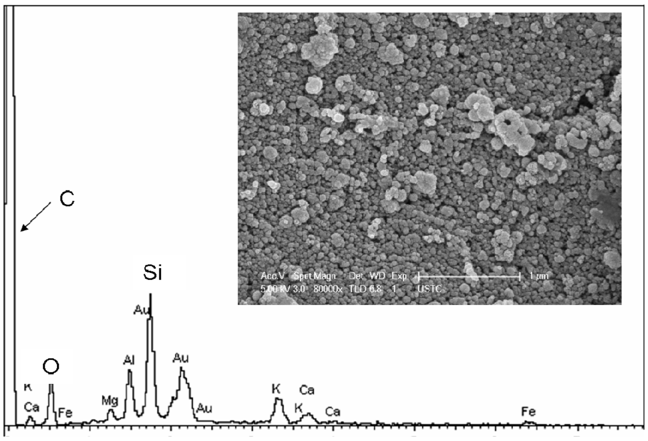

Figure 1. EDX analysis and SEM image (inset) of BCS.

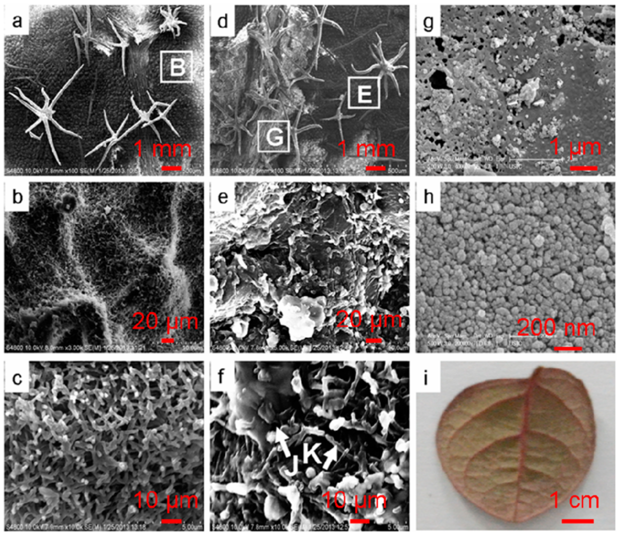

Figure 2. SEM images of the leaf surface (a), magnification of the square region labeled B in panel a (b), magnified image of panel b (c), BCS−CPF−leaf surface (d), magnification of the square region labeled E in panel d (e), magnified image of panel e (f), magnification of the square region labeled G in panel d (g), and BCS (h). Picture of the leaf was shown in panel i.

complexes (Figure 2e,f). Besides the networks, there were also plenty of starlike villi on the leaf surface (Figure 2a), which could be used as the barriers for BCS−CPF complexes (Figure 2d). Because of the housing effect of the networks and the barrier effect of the villi, BCS−CPF complexes could be retained on the leaf surface firmly, and thus the adhesion capacity of CPF on leaf surface increased.

To obtain the interaction between BCS and CPF, FTIR measurement of the BCS−CPF system were carried out. In Figure 3, peaks of CPF (1542 cm^{-1} for C═N, 1412 cm^{-1} for pyridine, 1017 cm^{-1} for C−O, and 965 cm^{-1} for P−O stretching vibrations) (Figure 3b) and BCS (789 cm^{-1} for Si−O−Si stretching vibration, 462 cm^{-1} for −OH translation, and 1094 cm^{-1} for Si−O stretching vibration) (Figure 3a) clearly appeared in the spectrum of BCS−CPF (Figure 3c), indicating the formation of BCS−CPF complexes. The existence of −OH on BCS probably implied the hydration of SiO_2 to form SiO_2−H_2O or H_2SiO_3. In addition, neither new peaks nor peak shifts were detected, indicating that new substances were not generated and obvious chemical reactions did not occur and that physical interaction mainly existed between BCS and CPF. It was proposed that part of CPF molecules might be adsorbed onto BCS through the hydrogen bonds formed between C−O or C−H of CPF and −OH or Si−O of BCS, whereas the rest of the CPF molecules might be adsorbed onto BCS through electrostatic attraction or surface potential energy.

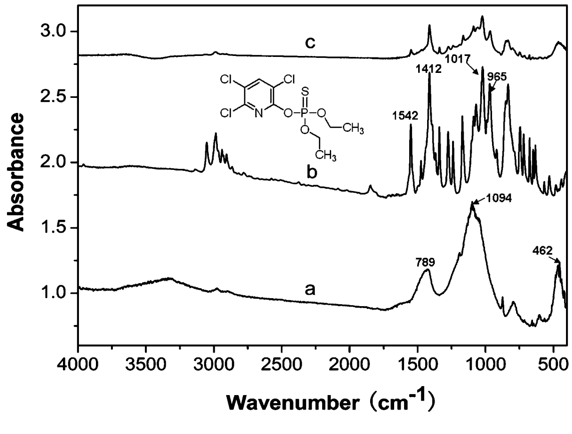

Figure 3. FTIR spectra of BCS (a), CPF (b), and BCS−CPF (c).

XRD measurement was performed to investigate the crystal-structure information of the LCC system. As seen in the XRD spectra (Figure 4), the characteristic peaks of both CPF (Figure 4d,e) and BCS (d = 3.3492 and 3.2220) could be found in the spectrum of BCS−CPF, which demonstrated that CPF was successfully adsorbed on BCS. Moreover, the peaks (d = 3.3472 and 3.1472) of BCS left-shifted to d = 3.3492 and 3.2220, respectively, after adsorption of CPF, illustrating that some CPF might intercalate the crystal layers in certain direction of BCS, resulting in a higher layer distance.

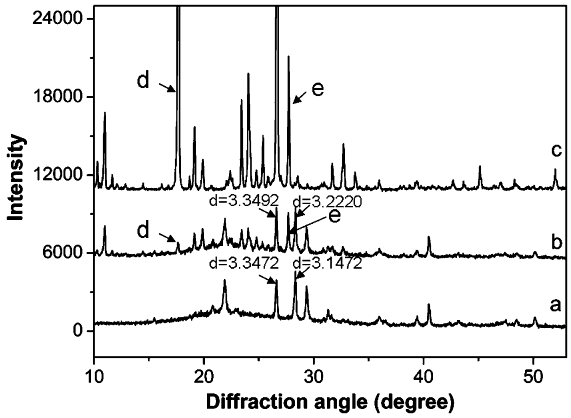

Figure 4. XRD spectra of BCS (a), BCS−CPF (b), and CPF (c).

3.2. Washing Loss Performance Investigation.

Because LCC could adhere more tightly to the leaf surface than CPF alone, LCC showed a higher antiloss ability. To compare conveniently the loss performance of LCC and CPF, the loss-control capacity of BCS (L_{BCS}) was used and defined as $L_{BCS} = (L_{CPF} - L_{LCC})/L_{CPF}$, where L_{CPF} and L_{LCC} refer to the loss ratio (loss amount/total amount on a leaf surface) of CPF and LCC, respectively. Furthermore, for loss through washing, leaching, and volatilization, their L_{BCS} were named L_{BCS-W}, L_{BCS-L}, and L_{BCS-V}, respectively.

The loss-control performance of LCC and CPF through both wet washing and dry washing were investigated. Wet washing could correspond to raining immediately after pesticide spraying, whereas dry washing reflected raining after the sprayed pesticide was dry. As shown in Figure 5A, L_{BCS-W} through wet washing and dry washing ranged from 14 to 24% and 11 to 23%, respectively, indicating that BCS could considerably reduce the washing loss of CPF through these two washing methods. In other words, BCS could effectively improve the adhesion ability of CPF on the leaf surface, resulting in a high antiwashing capacity and a low loss amount of CPF so that the utilization efficiency of CPF increased and then the applied amount of CPF could be reduced. The significant increase of the adhesion performance of CPF was mainly attributed to the high adsorption capacity of BCS and the retaining capacity of the rough structure of the leaf surface. However, no distinct relationship was found between L_{BCS-W} and BCS concentration, which was probably due to the varying particle size distribution of LCC (PSDL) under different BCS

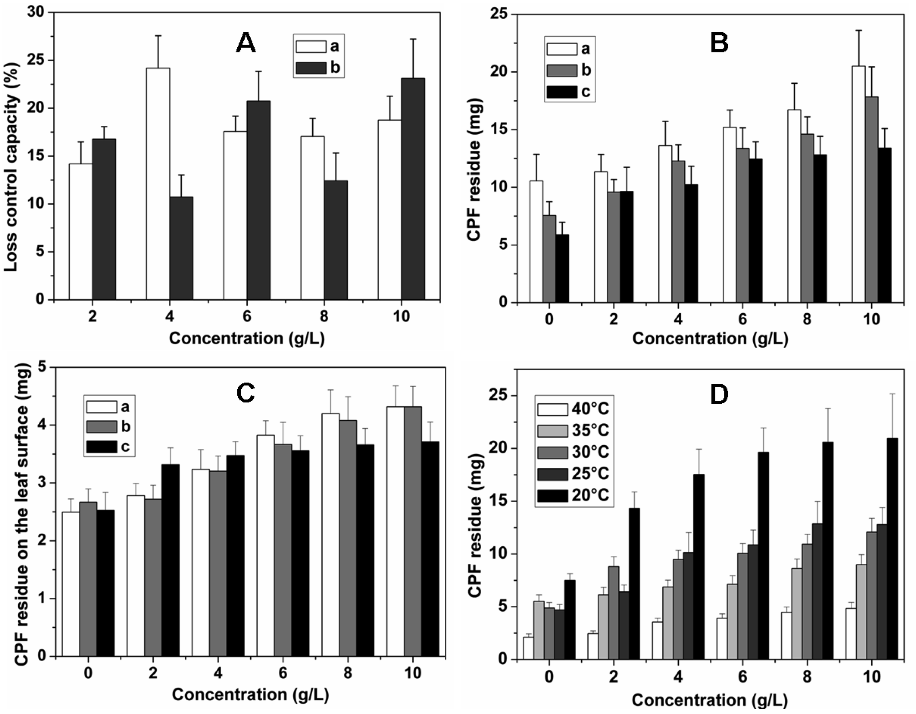

Figure 5. (A) Washing loss-control capacity of BCS with different concentrations of CPF (initial concentration of 4.8 g/L) from the leaf surface through wet washing (a) and dry washing (b). (B) Volatilization loss-control performance of BCS with different concentrations of CPF from emulsions at 15 °C under air flow velocities of 3.6 (a), 4.8 (b), and 6.0 km/h (c). (C) Volatilization loss-control performance of BCS with different concentrations of CPF (initial concentration of 4.8 g/L) from the leaf surface at 20 °C under air flow velocities of 3.6 (a), 4.8 (b), and 6.0 km/h (c). (D) Volatilization loss-control performance of BCS with different concentrations of CPF from emulsions at different temperatures under air flow velocities of 3.6 km/h.

concentrations that made it hard to match the pore-size distribution of the networks (PSDN) of the leaf surface regularly, resulting in irregular adhesion of LCC to the leaf surface. In other words, the dispersion of the LCC particles (actually the PSDL) varied with BCS concentration as well as the matching degree between the PSDL and PSDN, which played an important role in the adhesion behavior of LCC on the leaf surface (the higher matching degree, adhesion ability, and $L_{\mathrm{BCS-W}}$). Because of the complexity of the PSDL and PSDN, it was difficult for them to match each other regularly, resulting in an irregular matching degree as well as an irregular $L_{\mathrm{BCS-W}}$. Nevertheless, considering of performance/cost, the optimal BCS concentration for $L_{\mathrm{BCS-W}}$ through both wet washing and dry washing was 6 g/L.

3.3. Volatilization Loss Performance Investigation. Besides washing, another important route of pesticide loss is volatilization, which can induce not only a low utilization efficiency of pesticide but also severe contamination of the air. BCS could adsorb quite large amounts of CPF in the emulsion so that the volatilization amount of CPF could noticeably decreased, leaving more CPF in the emulsion compared with the control (without BCS), as seen in Figure 5B. The CPF residue increased with the increase of BCS concentration, because more CPF was adsorbed onto BCS. Furthermore, the CPF residue generally decreased with the air flow velocity, illustrating that the wind played an important role in the volatilization process of CPF.

BCS could also substantially control the volatilization loss of CPF from the leaf surface. From Figure 5C, it can be seen clearly that LCC possessed a much higher CPF residue on the leaf surface than the control did, wherein the residue increased gradually with the BCS concentration, which was attributed to the increasing adsorption amounts of CPF on BCS. Interestingly, when BCS concentrations were greater than 4 g/L, the CPF residue on the leaf surface decreased with the air flow velocity, which was similar to those from the emulsion (Figure 5B). However, when BCS concentrations were 2 and 4 g/L, the residues on the leaf surface exhibited different results, showing higher residues under a higher air flow velocity (6.0 km/h), which might be because the volatilization speed of CPF was affected by the volatilization speed of water. Moreover, such an effect could vary with the BCS concentration.

The volatilization of LCC from emulsions at different temperatures was also investigated, as shown in Figure 5D. The CPF residue amount in the emulsion of LCC was obviously higher than that of the control and increased significantly with the BCS concentration, which was also due to the adsorption behavior. Generally, the residue amount decreased with increasing temperature, except when BCS concentrations were 0 and 2 g/L. That is also probably because the volatilization speed of CPF was affected by the volatilization speed of water, and such an effect could also vary with the BCS concentration. This result demonstrated that temperature could influence the volatilization of CPF.

3.4. Leaching Performance of LCC in Soil. Pesticide washed onto the ground could leach underground, causing a prolonged degradation period of the pesticide, which is a huge risk for underground water pollution and a disaster for the microganisms in the soil. Hence, it is also important to control the leaching loss of the pesticide in the soil. The leaching loss performance of LCC was investigated compared with CPF. As seen in Figure 6B, LCC showed a quite high $L_{\mathrm{BCS-L}}$ that

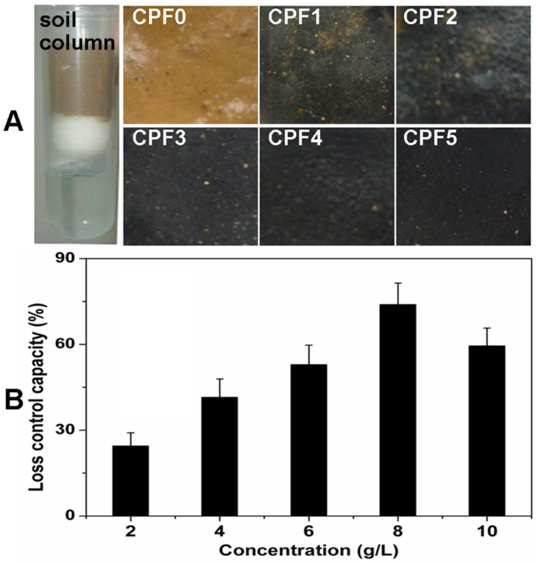

Figure 6. (A) Images of the soil column and the surface of the soil after leaching for different CPF samples. (B) Leaching loss-control capacity of BCS with different concentrations on CPF (initial concentration of 4.8 g/L).

increased from 28 to 75% with increasing BCS concentration. Therefore, BCS could significantly decrease the leaching loss of CPF. The higher BCS concentration, the better the leaching loss-control performance. This was because more BCS could adsorb more CPF, and the LCC particles could be retained by the soil layer because of the filtering effect, making the soil surface much more black compared with CPF alone (Figure 6A). However, when the concentration reached 10 g/L, BCS might aggregate, resulting in smaller specific surface area, a lower adsorption ability, and a smaller $L_{\mathrm{BCS-L}}$ compared with the concentration of 8 g/L. Obviously, through this loss-control technique, the leaching loss of CPF could be reduced and quite large amounts of the CPF could be retained in the top layer of the soil, which was favorable for the photolysis and biolysis of CPF thereafter. Additionally, such migration control of the pesticide in the soil was beneficial for the protection of the groundwater and microganisms in soil.

4. CONCLUSIONS

In this Article, an approach for controlling CPF loss was developed using LCC prepared by adding BCS to CPF. Because of the fine adsorption performance of BCS, the high retaining ability of the rough leaf surface, and the high filtering effect of the soil, LCC showed a significantly higher adhesion performance to the leaf surface and lower loss amounts through washing, leaching, and volatilization compared with CPF alone, which was closely related to the BCS concentration, wind speed, and temperature. This loss-control technique was beneficial for improving the utilization efficiency of pesticide and for reducing the environmental pollution risk.

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Notes

The authors declare no competing financial interest.

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