Effects of Spent Mushroom Compost on Degradation of Imidacloprid in Soil and Plant

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Abstract. The changes of imidacloprid content in contaminated soil and tomato plants were studied when the Spent mushroom compost (SMC) was added as environmental remediation material. Tomato planting experiment was carried out by applying SMC and chicken dung to soil containing imidacloprid at a ratio of 1:1, 0:1 and 1:0. A HPLC method was developed for the determination of imidacloprid in soil and tomato plants. The result is that the degradation rate of imidacloprid in the soil of SMC as substrate is faster, and its half-life is 11.2 days. The SMC have certain adsorption effect to imidacloprid, makes the imidacloprid content in tomato plants grown on the basis of SMC is lower. Thus the SMC can effectively promote the process of adsorption and degradation of imidacloprid in the soil.

1. Introduction
Imidacloprid is a new type of nicotinic insecticide, which is characterized by high efficiency, low toxicity, wide spectrum, strong internal absorption and long duration [1]. However, its wide application also leads to the detection of its residues in soil, atmosphere, groundwater and other environments in many countries and regions, which poses a potential threat to the environment [2, 3]. The spent mushroom compost (SMC) refers to the discarded culture medium which is cultivated and harvested from cotton seed husk, sawdust, straw, corn cob, bagasse and other crop stalks and industrial waste materials (such as wine lees, vinegar lees, molasses, waste liquid of paper mill, etc.) [4]. In recent years, the application of SMC as an environmental pollutant remediation agent is a new direction [5, 6]. The remediation of environmental pollutants by SMC mainly includes biodegradation and physical adsorption. On the one hand, the SMC has a huge specific surface area and a variety of functional groups that cause adsorption [7]. On the other hand, the SMC contains a variety of enzymes which can degrade pollutants in soil [8, 9]. In this paper, the degradation of imidacloprid pesticides in soil with the spent mushroom compost as the substrate and soil with chicken manure as the substrate were emphatically compared.
2. Experiment

2.1. Instruments and reagents

Instrument: Agilent 1100 High Performance Liquid Chromatograph, ultrasonic cleaner, low speed centrifuge, vortex instrument.

Reagent: Imidacloprid standard substance (purity: >99.9%, China Academy of Metrology); 10% imidacloprid wettable powder; sodium acetate, anhydrous sodium sulfate and sodium chloride were all analysed; methanol and acetonitrile were chromatographic pure; ultrapure water; 0.1% acetonitrile solution (acetonitrile contains 0.1% acetic acid); solid phase adsorption material for N-propyl ethylenediamine (PSA); C\textsubscript{18} sorbent.

Imidacloprid standard stock solution (1 mg/mL): accurately according to 100 mg of imidacloprid standard, dissolved in methanol, the capacity to 100 mL, -20\degree C storage.

The spent mushroom compost, chicken manure and soil used in the experiment were all from the oyster mushroom planting base in Fangshan District, Beijing.

2.2. Experimental scheme

The tomato planting experiment was carried out in the greenhouse of Beijing Academy of Agriculture and forestry sciences. Three groups of A, B and C were set as pot plants. The substrate of group A was SMC, the substrate of group B was chicken manure, and the substrate of group C was half of SMC and half of chicken manure. The ratio of soil to substrate in each group was 8:1. Each group included 30 pots, and each pot was treated with 10% imidacloprid wettable powder of 0.1g for tomato planting experiment. After the tomato seedling is planted, water will be poured through, and the sample will be sampled after two hours. Soil was collected at 1, 2, 3, 4, 5, 10, 15, 20, 30 and 40 days, respectively. The plants were collected on day 1, 3, 5, 7, 9, 11, 13 and 15. The content of imidacloprid in soil and tomato plants was tested in laboratory.

2.3. Experimental scheme

2.3.1. Working conditions of HPLC. Chromatographic column: C\textsubscript{18} column; Mobile phase: methanol: water: acetonitrile =55: 25: 20 (for soil); methanol: water = 60: 40 (for plant); Flow velocity: 1 ml/min; Sample intake: 20 kl; Column temperature: 30 \degree C; Detection wavelength: 270nm; Detection time: 15min.

2.3.2. Sample treatment. Soil: the soil sample was screened over 1mm, and 10g of the soil sample was weighed and taken in the 50mL screw cap centrifuge tube. 10g of anhydrous sodium sulfate and 1g of sodium acetate were added, shaken and mixed.15mL acetonitrile (containing 0.1% acetic acid) was added, and ultrasonic was applied for 20min. 2mL of supernatant was taken in a centrifuge tube preweighed with 100mgPSA and 50mgC\textsubscript{18}, which lasted for 30s. After 1min of centrifugation, the supernatant was taken, through 0.22 \mu m organic phase filter membrane, to be measured in the sample bottle.

Plant: cut and shred the plant sample into a mortar, add liquid nitrogen to grind, accurately weigh the 10g sample in the 50mL screw cap centrifuge tube. Add 15 mL acetonitrile, 5g anhydrous sodium sulfate, 1g sodium chloride, violently shake for 50s. After 20min ultrasound, remove the vortex and mix for 10s, centrifuge at the speed of 3800r/min for 5min. 2mL of supernatant was taken in the centrifuge tube preweighed with 50mg of anhydrous sodium sulfate, 100mgPSA and 50mgC\textsubscript{18}, and the supernatant was removed after being centrifuged for 30 seconds. After being centrifuged for 1min, the solution was removed and the solution was digested by 0.22\mu m organic phase filter membrane filter membrane before being measured in the sample bottle.

2.3.3. Linear range and detection limit. The reserve solution was diluted into a standard imidacloprid solution with a series of concentrations of imidacloprid: 0.010, 0.50, 1.0, 2.50, 5.0, 10, 50, 100\mu g/mL,
respectively. The retention time of imidacloprid was 2.78min and 8.32min, respectively, according to the chromatographic conditions in 2.3.1.

Taking the peak area as the ordinate (y), imidacloprid concentration as the abscissa (x), and for the condition that the mobile phase is methanol: water: acetonitrile = 55: 25: 20, the linear regression equation $y = 13.091x + 15.512$, $R$ squared = 0.9999, the standard curve is shown in fig. 1. For the condition that the mobile phase is methanol: water = 60: 40, the linear regression equation $y = 128.18x - 14.188$, $R$ squared = 0.9987 is obtained. The above indicates that the method has good linearity in the range of 0.1~500μg/mL. The standard imidacloprid solution was diluted stage by stage to 10 times the baseline noise at a concentration of 0.05μg/mL. If sampling 10 g, the minimum detection limit is 0.01 mg/kg.

![Figure 1. Imidacloprid standard curve.](image)

2.3.4. Recovery rate. Use the established method to process the blank soil sample and the labeled soil sample, and conduct liquid chromatography detection. The addition levels were respectively 0.5, 5, 25 and 100mg/Kg, and three parallel experiments were conducted for each sample. As show in Table 1, the results showed that the average recovery rate of imidacloprid in soil was 83.8%~90.8%, and the relative standard deviation was 2.46%~4.49%.

**Table 1. Recovery rate of imidacloprid in soil.**

| Addition level(mg/Kg) | Sample Concentration(mg/Kg) | Average recovery rate (%) | RSD (%) |
|-----------------------|-----------------------------|----------------------------|---------|
| **Imidacloprid**      |                             |                            |         |
| 0.5                   | 0.416                       | 83.8                       | 2.81    |
|                       | 0.409                       |                             |         |
|                       | 0.432                       |                             |         |
| 5                     | 4.58                        | 88.1                       | 3.47    |
|                       | 4.29                        |                             |         |
|                       | 4.35                        |                             |         |
| 25                    | 22.48                       | 86.6                       | 4.49    |
|                       | 21.89                       |                             |         |
|                       | 20.58                       |                             |         |
| 100                   | 90.8                        | 90.8                       | 2.46    |
|                       | 93.1                        |                             |         |
|                       | 88.6                        |                             |         |
Meanwhile, the recycling rate of tomato plant samples was tested at the level of 0.1 ~ 10mg/Kg, with the recovery rate between 85.3% ~ 98.9% and the relative standard deviation of 2.66% ~ 7.99%, meeting the requirements of national standard pesticide residue analysis.

3. Analysis and discussion Text

3.1. Imidacloprid content changes in soil

The content of imidacloprid in soil samples at different time can be used to visualize the degradation dynamics of pesticides in soil with different substrates. The degradation curve obtained by High Performance Liquid Chromatography (HPLC) is shown in figure 3. It can be seen from the diagram that the same concentrations of imidacloprid were added to the soil of different substrate, the SMC as substrate content of imidacloprid is 12.49mg/Kg higher than that of chicken manure. This may be because on the one hand, the SMC has certain adsorption to imidacloprid, on the other hand with chicken manure soil has a larger pore and higher permeability causing part of the pesticide with moisture loss. The content of imidacloprid in the three groups all decreased from 0 to 10 days, which was due to the degradation of pesticides in the soil. As can be seen from the figure, the degradation rate of imidacloprid in the soil based on SMC was significantly faster than that in the other two groups. The content of imidacloprid in the SMC group decreased by 34.62 mg/kg, while that in the other two groups decreased by 23.97mg/kg and 24.75mg/kg respectively. It may be related to the microorganism in the SMC that can promote the degradation of imidacloprid. The content of imidacloprid in the soil was basically stable after 20 days. On the 40th day, the content of imidacloprid in the soil based on the SMC was also at least lower 4.13mg/Kg than that in the other two groups, which indicated that the SMC had certain promoting effect on the degradation of imidacloprid and could effectively reduce the content of imidacloprid in the soil.

![Figure 2](image.png)

Figure 2. The content of imidacloprid in soil at different time.

Different Soil substrate first-order kinetic equation of degradation of imidacloprid is shown in table 2. It can be seen that the half-life of imidacloprid is 11.2d, 16.0d and 14.8d respectively in soil treated with SMC, soil treated with chicken manure and treated with half chicken manure and half SMC. The
addition of SMC can accelerate the degradation of imidacloprid in soil and lower the pesticide residues in soil.

Table 2. Resolution equation of imidacloprid in soil.

| Substrate    | Resolution equation | $R^2$ | Half life |
|--------------|---------------------|-------|-----------|
| SMC          | $C_t=48.42e^{-0.062t}$ | 0.96  | 11.2      |
| Chicken manure | $C_t=38.13e^{-0.043t}$ | 0.91  | 16.0      |
| 1:1          | $C_t=50.58e^{-0.046t}$ | 0.98  | 14.8      |

3.2. Changes of imidacloprid content in tomato plants
Changes in the content of imidacloprid in tomato plants are shown in the figure. As you can see, in the cultivation of 9 days, three groups of experiment plant absorption to imidacloprid were all reached the peak, but the SMC as a substrate of the experimental group, the plants of imidacloprid levels are lower than other two groups, it is only 5.38mg/Kg. This may be because on the one hand, the SMC have certain adsorption effect to imidacloprid, leading to the plant from the soil absorption of imidacloprid is reduced, on the other hand, due to the effect of promote the degradation of the microorganism in SMC, the imidacloprid concentration in soil of SMC group is significantly lower than the other two groups, so the uptake of tomato plants also less. For the experimental group with chicken manure as the substrate, the content of imidacloprid in the plants was significantly increased, reaching 6.67mg/Kg, which may be due to the weak adsorption capacity of chicken manure on imidacloprid, and the large amount of pesticide dissolved in water was absorbed by the roots of the plants. On day 15, the content of imidacloprid was also lowest in the SMC group. This suggests that planting crops in soil based on the spent mushroom compost can effectively reduce the content of imidacloprid pesticides in the plants, reduce agricultural residues and promote the healthy development of the plants.

![Figure 3](image-url)  
**Figure 3.** The content of imidacloprid in tomato plants at different time.

4. Conclusion
(1). Established a method for the determination of imidacloprid in soil and plant by HPLC. Different sample types use different liquid phase conditions to obtain different peak time, so as to better exclude the influence of impurities in soil and plants. The linear correlation of the method is good, and the accuracy and recovery meet the test requirements.

(2). The degradation rate of imidacloprid was significantly faster than that of the other two groups in the soil based on SMC, and the half-life was first reached, which is only 2 days. It indicating that
the addition of SMC promoted the degradation of imidacloprid. 40 days after imidacloprid was added, the SMC for substrate of imidacloprid in soil content is lower, it could be the result of physical adsorption and microbial degradation. The effect of SMC larger specific surface area and a variety of functional group can provide more adsorption sites. At the same time, the variety of microorganisms in SMC and the secretion of enzyme also played an important role to the degradation of pesticides.

(3). The content of imidacloprid was also significantly lower than that of the other two groups when tomatoes were planted in soil with SMC as the substrate. Indicating that the SMC not only promoted the degradation of imidacloprid in soil, but also had a certain hindering effect on the absorption of imidacloprid by plants.

(4). Microbial degradation is an important pathway for imidacloprid to migrate, transform and disappear in soil environment. In order to avoid the pollution of soil environment caused by imidacloprid in long-term use, it is necessary to further screen out the preponderant strains with strong degradation ability, so as to provide scientific theoretical basis for the remediation of contaminated soil.

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