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LÀM SẠCH CHLOROPHYLL TRONG LÚA TRƯỚC KHI PHÂN TÍCH TỒN DƯ HOÁ CHẤT BẢO VỆ THỰC VẬT BẰNG GC-MS

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Tóm tắt:

Khi phân tích bằng phương pháp sắc ký khí khối phổ, chlorophyll có trong mẫu sẽ gây ảnh hưởng xấu tới thiết bị, đặc biệt là ở buồng bơm mẫu, cột phân tích và detector khối phổ. Do vậy, loại trừ chlorophyll trong quá trình làm sạch mẫu trước khi phân tích trên thiết bị là một việc cần thiết. 4 loại than hoạt tính và các bon đen đã được sử dụng trong thí nghiệm loại bỏ chlorophyll. Kết quả chỉ ra rằng, chỉ có các bon đen (10 mg/mL) là phù hợp cho việc làm sạch chlorophyll mà vẫn đảm bảo tốt được độ thu hồi của các hóa chất bảo vệ thực vật cần phân tích.

Abstract:

Chlorophyll was known to have strongly harmful effect on the GC/MS system, especially on injector, column, and detector. Thus, minimization the amount of chlorophyll is the priority in cleaning step during sample preparation processes. Four types of granular activated carbon (GAC) and graphite carbon black (GCB) were used in this study to remove chlorophyll in the rice paddy sample. Results showed that only GCB (10 mg/mL) is suitable for both removal of chlorophyll and guarantee the acceptable recoveries of analyzed pesticides.

1. INTRODUCTION

Rice is a major food crop for more than 60 percent of the world's population. Rice also is an important nutrition source for not only Vietnamese but also for billions of people all over the world. Viet Nam is a tropical country, thus the pesticides of various kinds have been used on rice paddy fields to protect crops from damage inflicted by insects and diseases. Although intensively applied pesticides in rice paddy fields have increased grain production, its use has several drawbacks. Beside the high cost of the pesticides, the uses of pesticides may contaminate the products of field crops, as well as posing a serious danger to the environment (water, soil, and air pollution) and human health.

In order to help farmers control their crops productively with less effect to the environment as well as reducing pesticide residues in products, the Viet Good Agriculture Practices (VietGAP) program has been applied by farmers in Vietnam. Combining long-term perspective rice farming with VietGAP practices provides a sustainable alternative to rice cropping, from both an economic and an ecological point of view. On account of the potential risk to farmers when they apply pesticides to their crops as well as assessing the misuse of pesticides and the pesticide residues in the rice paddy (first stage of the late season period) there is a clear need for the analysis of pesticides in rice paddies.

Gas chromatography mass spectrometry (GC/MS) [1-2] is already well known for determination of pesticide residues. Actually, the sample to be analyzed by this technique requires as low as possible of the interferences remaining in the sample that may effect to GC system, quantitation, and identification's works. Chlorophyll gives rice paddies their green color. These colors have been known to have strongly harmful effect to the GC system, especially on injector, column, and detector. Thus, minimization the amount of color is the priority in cleaning step during sample preparation processes. Granular activated carbon (GAC) and graphite carbon black (GCB) are known compounds being used to remove color. In contrast, the uses of GAC and GCB as absorbents may also absorb the target compounds such as pesticides with planar structures. Therefore, the application of using GAC or GCB as absorbent for the removal of chlorophyll should be thoroughly studied. In this study, four types of GAC and GCB were used in color removal experiments.

2. EXPERIMENTAL

2.1 Chemicals

The standard pesticides were purchased from Wako (Osaka, Japan), Chemservice (West Chester, PA, USA) and Dr. Ehrenstorfer (Ausberg, Germany). The purities of the standard pesticides were from 97.4% to 99%. Internal standards were purchased from C/D/N Isotopes INC. (Quebec, Canada) and Chemservice (West Chester, PA, USA). All solvents were pesticide analytical grade and were purchased from J.T. Baker (Philipsburg, NJ, USA). The 18MΩ-purified water was achieved by Ultra-pure water (Sinhan Science Tech, Daejeon, Korea). Anhydrous $MgSO_4$, NaCl, $(NH_4)_2S_2O_8$ and H_2SO_4 were obtained from Wako (Osaka, Japan). Graphite carbon black was obtained from Supelco (Bellefonte, PA, USA). Four types of granular activated carbon (ACF-Nanotech, UFG, AFC-Anshan and AFC-Anshane) were obtained from Shinyo Pure Chemicals, Shinki Company, Japan and Anshan Company, Korea.

2.2 Instrumentation

A Shimadzu 2010 gas chromatograph equipped with a split-splitless auto-injector model AOC-20i, an auto sampler model AOC-20s and a MS-QP 2010 series mass selective detector was used for the analysis of the studied pesticides. A fused silica capillary column, 5% phenyl polysiloxane as non-polar stationary phase (30 m x 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Agilent was used for the GC separation.

A Shimadzu UV-Vis spectrometer was used for the analysis of chlorophyll in extracted samples.

2.3 Preparation of GAC before used

GAC was washed with H_2O for 2 days and boiled in H_2O for 2 hours. It was then dried overnight in oven at 110 ^{o}C and then stored in desiccator.

$(NH_4)_2S_2O_8$ pre-treatment: GAC was oxidized with a saturated solution of $(NH_4)_2S_2O_8$ in H_2SO_4 1 M (1 g carbon equal with 10 mL solution) at 25 ^{o}C for 24 hours, then washed with hot distilled water to neutral pH.

After pre-treatment, GAC was washed thoroughly in hot distilled water and dried overnight in oven at 110 ^{o}C and then stored in desiccator till further use.

GCB was used directly without preparation.

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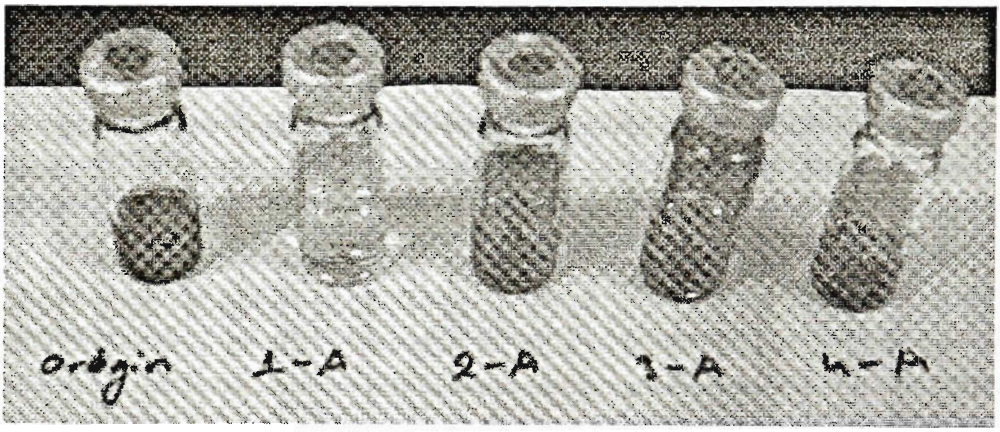
2.4 Sample Preparation

Rice paddy sample was extracted by MeCN followed procedure as described previously [3]. Sample extracts were applied with GAC and GCB at concentrations of 5, 10, 15 and 10, 15, 20, 25, 30 mg/mL of the extract, respectively. Then, the extracts were analyzed by GC/MS as previously described [3].

3. RESULTS AND DISCUSSION

3.1 Effect of Mass of Granular Activated Carbon on the Removal of Chlorophyll

The effectiveness of the removal of chlorophyll by four types of GAC was observed by eye as presented in Figure 1. UFG and ACF-Anshane types showed the first and the second in the removal of chlorophyll as clearly observed in Figure 1.



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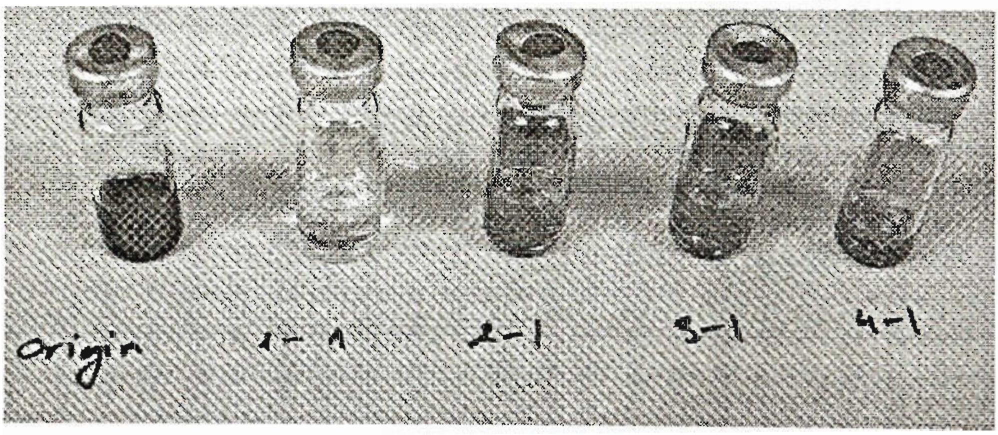

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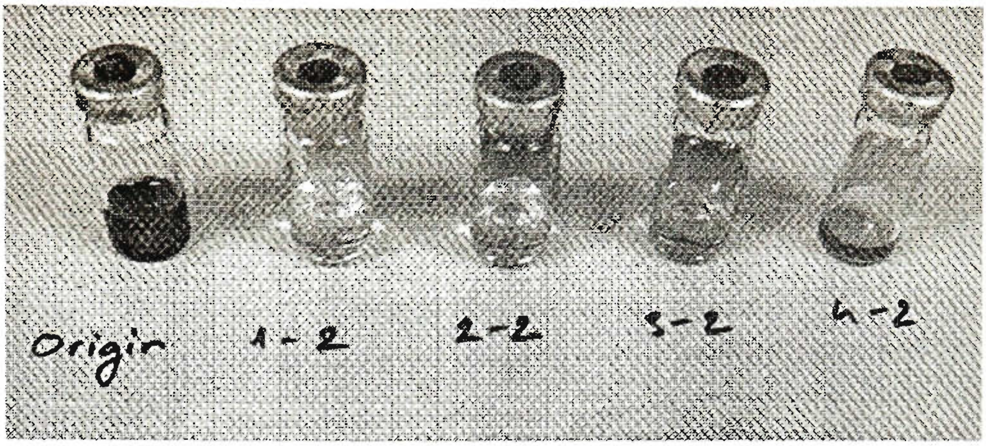

1-3

Figure 1: Effect of mass of H_2SO_4 treated GAC on the removal of chlorophyll

1-1: 5 mg/mL of UFG (1-A), ACF-Anshane (2-A), ACF-Anshan (3-A), and ACF-Nanotech (4-A);

1-2: 10 mg/mL of UFG (1-1), ACF-Anshane (2-1), ACF-Anshan (3-1) and ACF-Nanotech (4-1);

1-3: 15 mg/mL of UFG (1-2), ACF-Anshane (2-2), ACF-Anshan (3-2), ACF-Nanotech (4-2).

Based on the experiment result, the UFG and ACF-Anshane were selected for further experiment. Standard solution was spiked to the samples to reach the concentration of 1 mg/kg. Then, the samples were extracted, cleaned to remove chlorophyll by two types of GAC and injected to GC/MS. Results (Figure 2) showed that none of them could be applied to the cleaning step due to their absorption of not only chlorophyll but also target compounds.

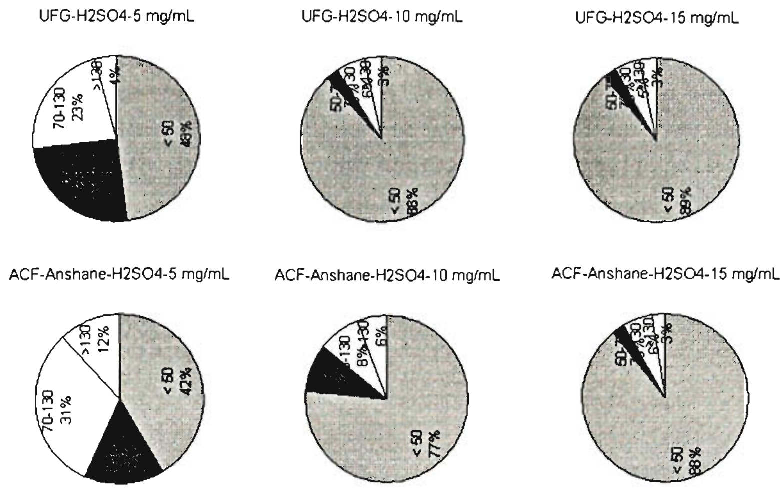

Figure 2: Effect of GAC on the Recovery of Pesticides

3.2 Effect of Mass of GCB on the Removal of Chlorophyll

The effects of the mass of GCB on the removal of chlorophyll was tested in order to find out the suitable amount of GCB used in the cleaning step that could remove as much chlorophyll as possible in rice paddy samples. The effectiveness of the removal of chlorophyll was observed by UV spectrophotometer at 410 and 480 nm. Figure 3 showed that most chlorophyll was removed when 10-15 mg/mL GCB is applied.

Although the uses of GCB in the removal of chlorophyll showed good results, losses of certain compounds such as low polarity and planar structure pesticides may also occur during cleaning processes.

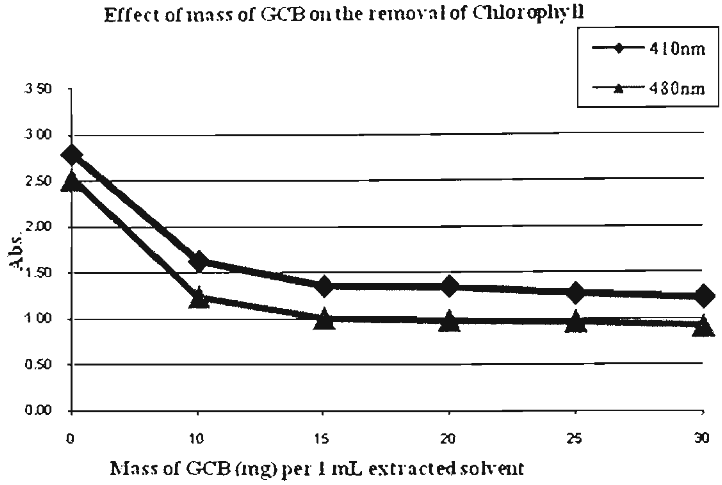

Figure 3: Effect of Mass of GCB on the Removal of Chlorophyll

Then, low polarity and planar structure pesticides (alachlor, bromacil, chlorothalonil, chlorpyrifos, dichlorobenil, parathion, pendimethalin, quintozene, and terbufos) were selected for further study to confirm no unacceptable losses of pesticides when these amounts of GCB were applied. The standard mixed solution of these pesticides was spiked into the rice paddy sample extracts and then 3, 6, 9, 12 and 15 mg/mL of GCB were added. After being vortexed and centrifuged, the extracts were transferred to GC vials for GC/MS recovery determination. Figure 4 showed that with 15 mg/mL of GCB, recovery yields of chlorothalonil and quintozene were below 60%; with 12 mg/mL of GCB, quintozene showed the recovery yield lower than 70%; and with GCB treated at 9 mg/mL, all studied pesticides achieved recovery yields higher than 70%. Thus, it is concluded that 10 mg/mL of GCB can be applied to remove chlorophyll in rice paddy sample without strong effect on the recovery yield of analyzed pesticides.

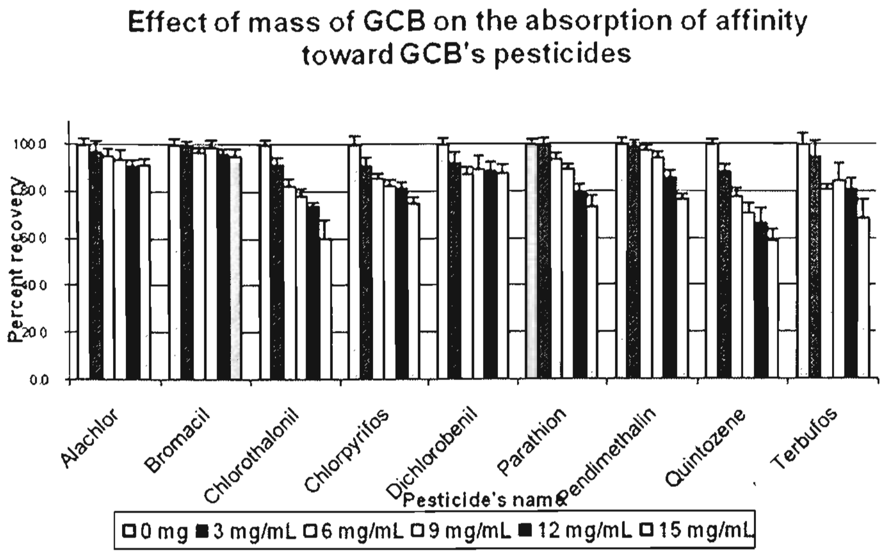

Figure 4: Effect of Mass of GCB on the Absorption of Affinity toward GCB's Pesticides

4. CONCLUSIONS

Granular activated carbon and graphite carbon black can be used to absorb chlorophyll in the rice paddy sample. Among these absorbents, only GCB at 10 mg/mL showed good result for not only removing the chlorophyll but also giving no signification effect on the recovery yield of analyzed pesticides.

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