

# INTRODUCTION

## 1. Reasons to choose the subject

Environmental pollution is a matter of global concern and concern. With the rapid and rapid development of the current situation in all areas of human life, more and more hazardous wastes are introduced into the natural environment.

In particular, there are many pollutants that cause cancer, causing serious damage to the environment and human health such as metal elements iron, lead, mercury, copper, organic compounds of phenol and chlorine derivatives of benzene. Typically, POPs contain persistent plant protection chemicals in the air, water and soil at the store of pesticides have long been unused. At present, although modern methods of tools have been developed, direct disposal and disposal of pollutants in contaminated soils is difficult. The treatment of these compounds, from collection to decomposition to no secondary pollutants, encounters many obstacles and challenges in the treatment of soil that is contaminated with pesticide residues. long time. Moreover, funding for implementation is quite high compared to the developing economy of Vietnam. Therefore, the treatment of agricultural soil is contaminated with plant protection chemicals, especially DDT, DDD, DDE by easy-to-apply methods, low cost and in line with Vietnam's current conditions are very necessary.

Polyaniline (PANi) is one of the materials studied by scientists for a long time. It is highly valuable because it is relatively easy to manufacture, stable, durable, environmentally friendly, easy to handle. doped, denatured and doped to improve, add the necessary characteristics, in the direction of application of materials. In particular, PANi has been used effectively to absorb some organic pollutants, heavy metals such as Pb, Fe, Cr,... This is the main advantage of PANi, with the characteristics can be doped, denaturing, thereby increasing the ability to absorb environmental pollutants, especially organic pollutants that pollute the environment, Chlorophenol derivatives include chloroform, dicryl diphenyl trichlorethane (DDT), dichlorid diphenyl dichloride (DDD), dichlorid diphenyl diclorethylene (DDE)....

At present, the materials are agricultural waste such as coconut fiber and sawdust, this is a source of renewable materials, cheap, easy to find in Vietnam and they all have the ability to absorb heavy metals and some other organic compounds that pollute the environment. The studies on the adsorption capacity used to treat environmental pollution have been investigated in the PANi material, sawdust and coconut fiber, suggesting the synthesis of PANi material on sawdust carriers and coconut fiber for

adsorption applications DDT, DDD, DDE is a new direction and can be applied in Vietnam.

Therefore, I chose the thesis topic as: *“Study on synthesis of polyaniline-based materials oriented for adsorbing DDT extracted from contaminated soil”*

## **2. Research objectives**

Separation of DDT, DDD and DDE compounds from contaminated agricultural land.

Synthesize and investigate the properties of the PANi conductive polymer material on sawdust and coir chemical polymerization.

Examination of the adsorption capacity of DDT, DDD, DDE in soil extracts contaminated with PANi/sawdust and PANi/coir in different conditions.

From this, the isothermal adsorption models of the DDT adsorption process of PANi conductive polymer material on sawdust and coir are presented.

## **3. Research content**

Study on separation of DDT compounds from contaminated soils by extraction with organic solvents including straight chain alcohols to obtain solutions containing DDT

Study on the synthesis of PANi materials on sawdust and coir at the mass ratios of aniline as compared to sawdust and coir.

Analysis of basic structural characteristics of PANi materials through infrared spectroscopy (IR) and scanning electron microscopy (SEM)

Research on the adsorption capacity of DDT compounds (including DDT, DDE, DDD) in soil extracts from contaminated soils with different conditions such as the nature of adsorbents, adsorption time, mass of adsorbed material and initial concentration of adsorbed material.

Study and investigate the adsorption balance of DDT, DDD, DDE compounds by conductive PANi/ coir material under Langmuir and Freundlich adsorption models.

## **4. The scientific and practice meanings of the thesis**

### ***Scientific meanings:***

The results of this thesis contribute to the use of organic solvents to extract DDT compounds from polluted soils with solvent systems containing alcohol, it is the scientific basis for the application of the treatment of soil contaminated with pesticides.

Particularly, the dissertation also contributed to clarify the adsorption process of DDT, DDD, DDE compounds of polyaniline base materials synthesized on sawdust and coir.

From the adsorption results, it is possible to determine the adsorption capacity of DDT by PANi material according to the Langmuir and Freundlich isothermal models.

***Practice meanings:***

The research results of the thesis is the scientific basis for the application of organic solvents containing alcohol to handle the removal of DDT, DDD, DDE, this is common pesticide residues and most typical of pesticide contaminated soil in Vietnam today

The result of the thesis is also the basis for the use of PANi materials hybridized with sawdust, coconut fiber in the treatment of the environment in water containing the organic compounds difficult to decay as pesticide chemicals, dye organic pollutants, heavy metals polluting the environment, ...

**5. Object and scope of the study**

*Research subjects:*

DDT contaminated soil is collected in Hon Tro – Nghe An.

Polyaniline, sawdust and coir.

*Research scope:*

Extract and clean soil samples contaminated with DDT collected in Hon Tro - Nghe An.

Synthesis of PANi/ coir and PANi/ sawdust materials capable of adsorbing persistent organic plant protection chemicals (DDT, DDD, DDE) extracted from contaminated soil..

Adsorption of DDT compounds from contaminated soil extracts, removal of DDT from extracts to recycle solvent.

**6. Layout of the thesis**

The thesis consists of 143 pages which is divided to following sections: Introduction: 4 pages; Chapter 1. Overview: 35 pages; Chapter 2. Research Methodology and empirical: 20 pages; Chapter 3. The results of research and discussion: 67 pages; Conclusions and Recommendations: 2 pages; New points of the thesis: 1 page; All works published related to the thesis: 2 pages; References 12 pages; The thesis consists of 24 tables, 91 figures and 119 references.

# MAIN CONTENT

## CHAPTER 1: OVERVIEW

### Overview studied in 119 references, namely:

- 1.1. The status of chemical pollution of organic plant protection is difficult to decompose
- 1.2. Polyaniline polymer and application
- 1.3. Overview of coir and sawdust
- 1.4. Adsorption methods
- 1.5. Oriented research thesis

## CHAPTER 2. EXPERIMENTS AND METHODOLOGY

### 2.1. Equipment and chemicals

Chemicals, tools and equipment used in the entire thesis is pure chemical sources originating from China, Germany, Japan, Italy, Poland and Vietnam.

### 2.2. Experiment

#### 2.2.1. *Principle polluted soil sampling*

- Soil samples in Hon Tro (Dien Yen, Dien Chau, Nghe An), as one of the most seriously contaminated areas of pesticide chemicals in accordance with Decision No 1946/QĐ-TTg dated 21/10/2010 of the Prime Minister should be handled.

- The sampling of land for study, preservation and safe transportation of samples in accordance with the regulations on land sampling methods studied to determine residues of plant protection chemicals, is taken on topsoil according to Vietnamese standards TCVN 5297: 1995 - soil quality - sampling - general requirements; TCVN 7538-2: 2005 - Soil Quality - Sampling - Part 2: Guidance on Sampling Techniques and Circular No. 33/2011 / TT-BTNMT dated 15 September 2011 by the Ministry of Natural Resources and Environment of Vietnam.

#### 2.2.2. *Extraction of pesticides from contaminated soil*

##### 2.2.2.1. *Method to create solvent system for extraction*

Purpose: The objective of the thesis is to assess the ability of DDT compounds to be processed by PANi materials. Specifically, a solution containing pesticides, including DDT, DDD, DDE, is obtained. In order to ensure the scientific and practical conditions, the study on the extraction of

plant protection chemicals (DDT, DDD, DDE) from contaminated soil by various organic solvents, is conducted to ensure the progress of the thesis.

Solvent extraction systems, jointly developed by PhD student and the research team of the Institute of Energy Science and the Institute of Tropical Technology - Vietnam Academy of Science and Technology, together with the staff of the Faculty of Chemistry - Hanoi Pedagogical University No.2 together study and calculated to prepare QH solvents for extraction. Major solvent extraction systems include straight chain alcohol such as ethanol (C<sub>2</sub>H<sub>5</sub>OH), butanol (C<sub>4</sub>H<sub>9</sub>OH), butane-1,3-diol (HO-C<sub>4</sub>H<sub>8</sub>-OH), ... mixed with distilled water in different proportions, forming three solvent systems are QH1, QH2 and QH3 respectively.

When extracting DDT compounds from contaminated soils, these solvent systems are diluted with distilled water (Table 2.1). In addition, solvent systems are added with a small amount of environmentally friendly and non-polluting additives, the purpose is to prevent the formation of dirt, stains due to clay particles in the soil, and the addition of solvent as an additive to emulsify the DDT compounds and dispersed well in solvent systems. Therefore, these QH solvents have the ability to dissolve DDT compounds at different levels, so they can be separated from contaminated soils at different levels of extraction.

Solvent systems QH1, QH2, QH3 after being studied in the laboratory and achieving high results in extracting DDT from contaminated soil (results are presented in articles published in the Journal of Chemistry. learn) and was approved by the project management unit "*Building capacity to eliminate POP pesticides stockpiles in Vietnam*" of the Ministry of Natural Resources and Environment to treat contaminated soil in Hon Tro - Nghe An, under the close supervision of experts from the Ministry of Natural Resources and Environment and foreign experts.

These extraction solvent systems are formulated in different proportions of the percentages by volume of solvents QH1, QH2, QH3 and water, as shown in Table 2.1.

*Table 2.1. The different QH extraction solvent systems*

<b>%V-QH1</b>	<b>Symbol</b>	<b>%V-QH2</b>	<b>Symbol</b>	<b>%V-QH3</b>	<b>Symbol</b>
0.0	QH1-0	0.0	QH2-0	0.0	QH3-0
5.0	QH1-5	5.0	QH2-5	2.5	QH3-2.5
10.0	QH1-10	10.0	QH2-10	5.0	QH3-5
15.0	QH1-15	15.0	QH2-15	7.5	QH3-7.5
20.0	QH1-20	20.0	QH2-20	10.0	QH3-10
25.0	QH1-25	25.0	QH2-25	15.0	QH3-15

30.0	QH1-30	30.0	QH2-30		
35.0	QH1-35	40.0	QH2-40		

The solvent systems after mixing are stirred and stored for at least 30 minutes so that the substances are dispersed evenly in water.

Each solvent system QH1, QH2, QH3 is taken with volume  $V = 300$  ml and then divided into 3 equal parts to proceed with 3 successive extractions in each sample has a mass of 100 grams

#### 2.2.2.2. *Soil sample preparation and extraction system*

The soil samples were analyzed for moisture content before study, the mean value ranged from  $14 \div 16\%$ .

Soil samples are mixed then mechanically ground, the average soil particles are  $1 \div 3$  mm. If the grain is too small it will reduce the flow rate and if too big will reduce the speed of the extraction. When stuffing the soil into the column just to lay out naturally, do not compress.

Mount the column upright and wash it with distilled water and place it on the iron rack. Then put in the extraction column with the order of materials as follows:

*Smooth lining 1 (cotton) → Lining porous (rock) → smooth lining 2 (cotton) →  
→ Soil samples → coatings smooth (cotton) → Overlay Positioning (rock)*

#### 2.3.3. **Synthesis material PANi, PANi/coir and PANi/sawdust**

Materials PANi, PANi/ sawdust and PANi/ coir with the ratio of the initial mass of Ani and coir or sawdust =  $1/0$ ;  $2/1$ ;  $1/1$ ;  $1/2$  is synthesized by chemical methods in acidic  $H_2SO_4$  and uses persulfate ammonium oxidizing agent, the reaction is carried out for 15 hours, at a temperature between  $0 \div 5^\circ C$  on a magnetic stirrer. After the end of the experiment, PANi was washed several times with water to the neutral pH and further washed with acetone solution to remove all residual Ani. Finally, it was dried at a temperature of  $70^\circ C$  PANi in the oven. PANi weight scale, aggregated performance properties were preserved in jars sealed in plastic PANi and desiccator. After synthesis was complete, we achieved the following materials PANi, PA/XD21, PA/XD11, PA/XD12, PA/MC21, PA/MC11, PA/MC12.

In addition to the materials synthesized above, the DDT adsorption process also uses some of the materials by mechanical mixing of the PANi material with sawdust (MC), coir (XD) and activated carbon (THT) after synthesis is PANi, is denoted PANi+MC, XD and PANi, PANi+THT (PA+MC, PA+XD, PA+THT).

#### 2.3.4. **Research adsorption capacity of the original materials PANi**

Synthetic materials have been used to study the absorption of organic pesticides persistent organochlorine formed by the original conductive

polymer materials synthesized Pani in different conditions such as impact characteristic elements of the original adsorbent fibers PANi with melon, sawdust; the effects of different rates of weight with coconut fiber monomers ani and sawdust; the influence of adsorption time; the influence of adsorbent volume PANi original; and the effect of adsorbed concentrations of pesticides containing organic chemicals persistent.

### 2.3. Research Methods

The research methods and morphological structure of the original conductive polymer materials synthesized PANi (infrared spectroscopic methods, scanning electron micrographs).

Extraction method for the extraction of pesticides washed off the contaminated soil and gas chromatography mass spectrometry (GCMS) for analysis to determine the amount of pesticides in contaminated soil, wash liquid extraction, absorption solution.

## CHAPTER 3. RESULTS AND DISCUSSION

### 3.1. Extraction of pesticides from contaminated soil

#### 3.1.1. Levels of pesticide chemicals extracted from soil

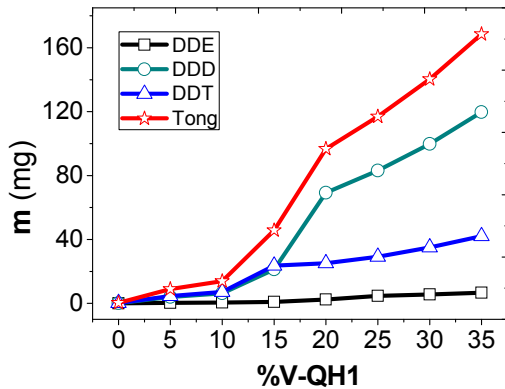


Figure 3.1. The total quantity of substances extracted by solvent QH1

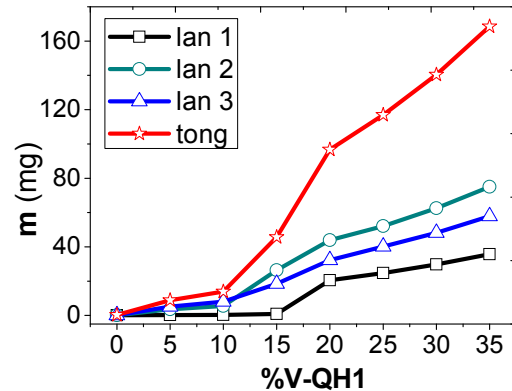


Figure 3.2. POP at the time the amount extracted by solvent QH1

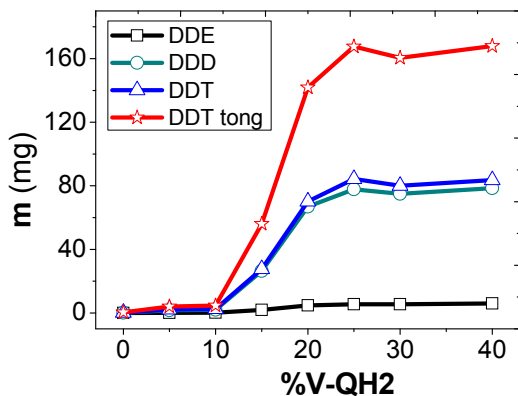


Figure 3.4. The total quantity of

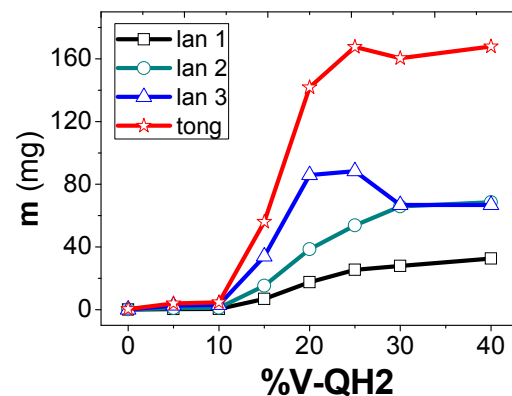


Figure 3.5. POP at the time the

substances extracted by solvent QH2

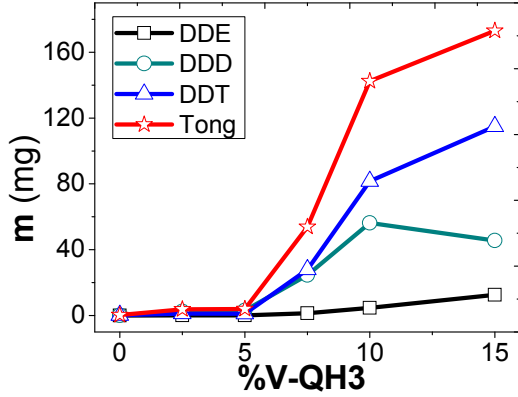


Figure 3.7. The total quantity of substances extracted by solvent QH3

amount extracted by solvent QH2

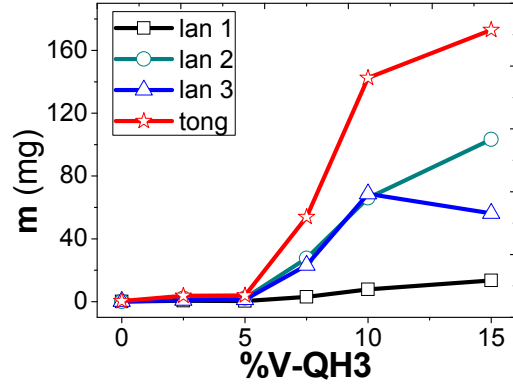


Figure 3.8. POP at the time the amount extracted by solvent QH3

### 3.1.2. Comparing the ability of the solvent extraction

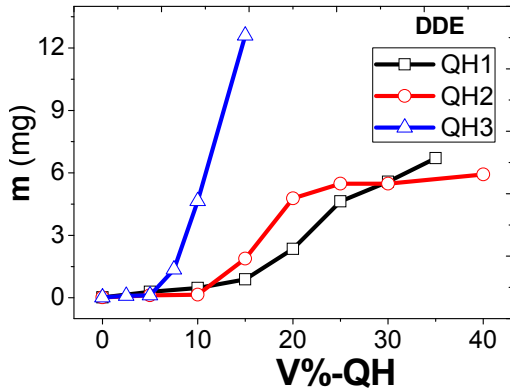


Fig 3.10. The total amount of DDE extraction of solvents

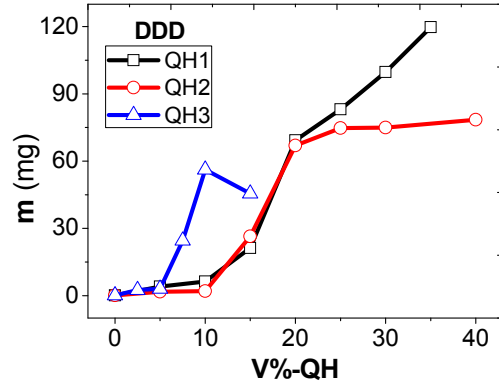


Fig 3.11. The total amount of DDD extraction of solvents

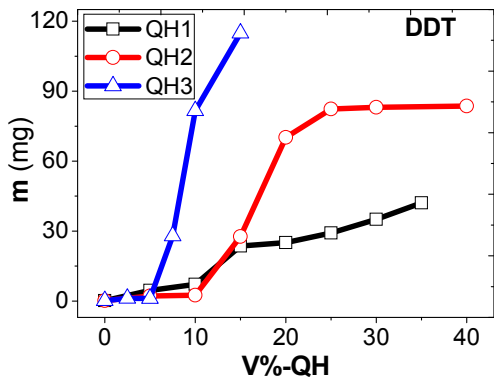


Fig 3.12. The total amount of DDT extraction of solvents

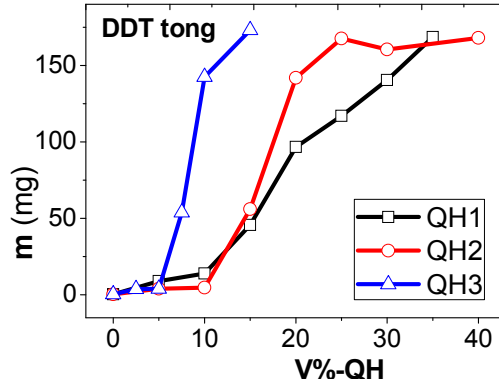


Fig 3.13. POPs in the amount of 3 times the extraction solvent



### 3.1.3. So sánh tỉ lệ khối lượng các chất POP tách chiết được

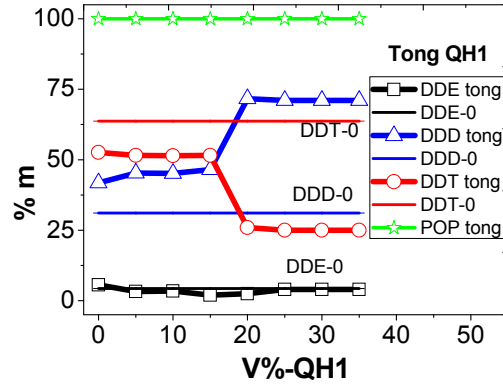


Figure 3.17. The ratio of total DDT substances extracted by QH1

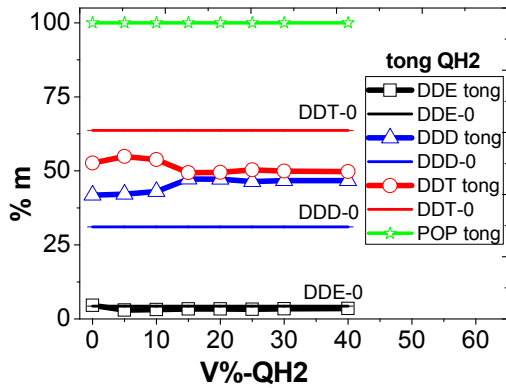


Figure 3.21. The ratio of total DDT substances extracted by QH2

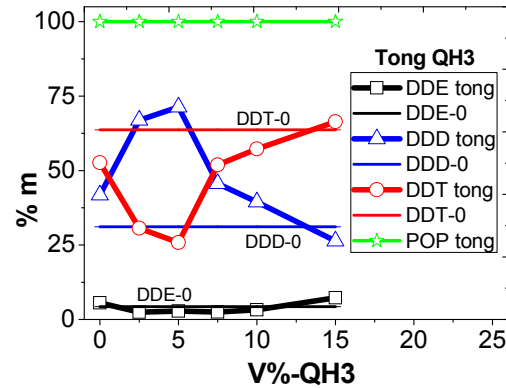


Figure 3.25. The ratio of total DDT substances extracted by QH3

From the results of the pesticide chemical extraction in Section 3.1, can offer a number of conclusions:

- The ability of solvents extraction for each substance: For QH1 solvents extraction ability of compounds DDD > compounds DDT > compound DDE, solvent extraction QH2 possibility of compounds DDT  $\approx$  compounds DDD > compounds DDE and solvents for extraction QH3 possibility of compounds DDT > compounds DDD > compound DDE.
- The extractability of the extracted DDE compounds in QH3 > QH1 > QH2, with DDH compound QH1 > QH2 > QH3, and for compound DDT QH3 > QH2 > QH1. Finally, the total DDT extraction capacity of QH3 > QH2 > QH1.
- Solvent systems QH1, QH2, QH3 are capable of extracting DDT compounds with high efficiency. Which, the DDD compound is capable of being extracted with the highest concentration.
- The mass ratio of the components after extraction is varied relative to their initial mass ratio in the soil. This suggests that QH solvents change their ratio from compound DDT to DDD to increase the mass ratio of DDD and decrease the mass ratio of DDT. From the data extracted DDT,

DDD, DDE, we can calculate the level of conversion of DDT compound to DDD compound by QH solvent systems from 2% to 58.89%.

- Based on the above results, the solvent system selected for further experiments is the 15% QH3 solvent system to separate the DDT from the contaminated soil. For the reason: **Firstly**, the solvent system QH1, QH2 must be used at high concentrations from 35% (with QH1) and from 25-40% (with QH2) has a separation efficiency of more than 90%, so it will take more solvent and funds for processing. **Secondly**, at a low concentration of 15% QH3, the extraction efficiency was more than 95%, thus reducing the solvent used and reducing the processing cost.

### 3.2. Synthesis polyaniline material (PANi)

#### 3.2.1. Synthesis performance of polyaniline materials

Synthetic efficiency was calculated using the formula:

$$\% H = \frac{m_1 - m_2}{m_3} 100\%$$

Where:  $m_1$  is the mass of the PANi material (gam)  
 $m_2$  is the mass of the substrate (coir - sawdust) (gam)  
 $m_3$  is the mass of the ANi monomer (gam)

From the facts of the synthesis of the original materials are processed PANi denaturation and hybridization with sawdust coir we obtain the aggregate performance of the materials in Table 3.1.

The result of the overall performance of original material absorbs PANi/coir, PANi / sawdust was high, aggregated performance rules increases as the rate of increase of the monomer volume compared with the volume of Ani Coir or sawdust.

*Table 3.1. Metabolic performance aniline absorbed into the original material PANi*

Material	ANi:coir ANi:sawdust	$m_1$ (g)	$m_2$ (g)	$m_3$ (g)	Performance (%)
PANi	1:0	5,00	0	4,60	92,00
PANi/ coir	2:1	13,99	5,00	10,00	89,90
	1:1	9,30	5,00	5,00	86,00
	1:2	14,16	10,00	5,00	83,20
PANi/ sawdust	2:1	27,85	10,00	20,00	89,25
	1:1	9,32	5,00	5,00	86,40
	1:2	28,55	20,00	10,00	85,50

### 3.2.2. The results of analysis of materials by infrared spectrum (IR)

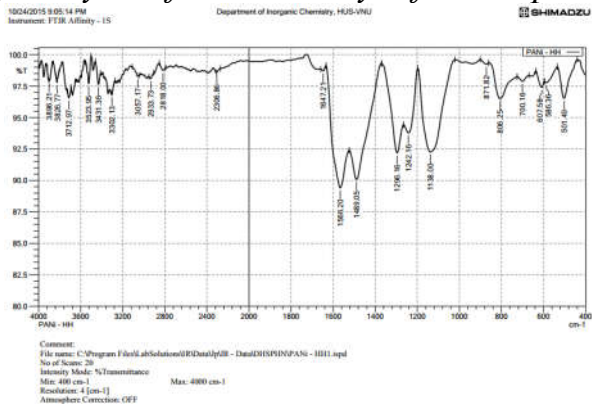


Fig. 3.26. PANi infrared spectrum synthesized by chemical methods

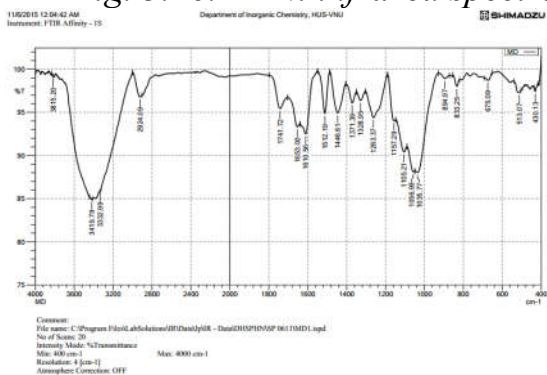


Fig. 3.28. IR spectra of coir

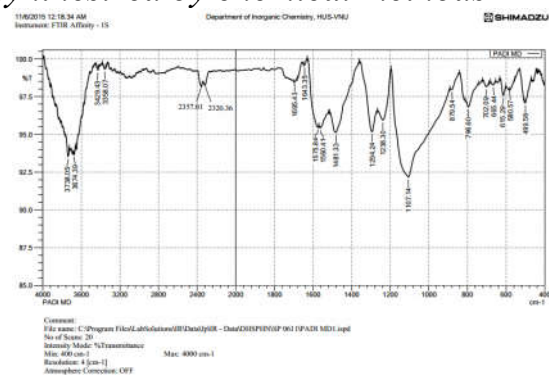


Fig 3.29. Infrared spectral absorption of original material PANi/ coir

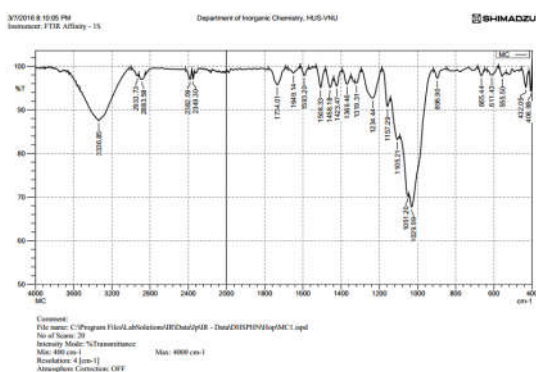


Fig. 3.31. IR spectra of sawdust

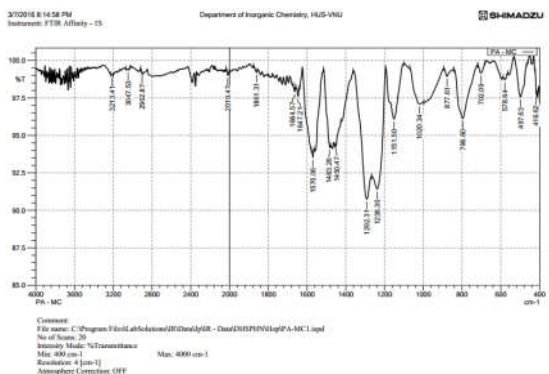


Fig 3.32. Infrared spectral absorption of original material PANi/ sawdust

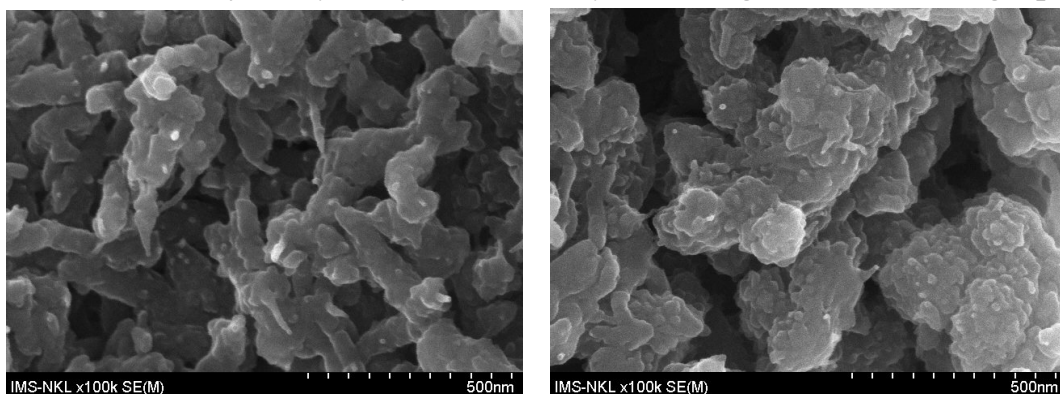
Infrared spectroscopic analysis of the material obtained shows the characteristics of the material, in particular: For the material sawdust and coconut fiber signals appear specific to cellulose compounds, lignin. Also in the spectrum of the original materials PANi, PANi/ coir, PANi/ sawdust signals also appear typical of compounds PANi and in coconut fiber and sawdust, which proved to be synthetic and Pani government on coir material

and sawdust. All the data on the infrared spectrum of the material PANi, are shown in the following table 3.2.

*Table 3.2. Attributed to the typical pattern for the infrared spectrum of materials*

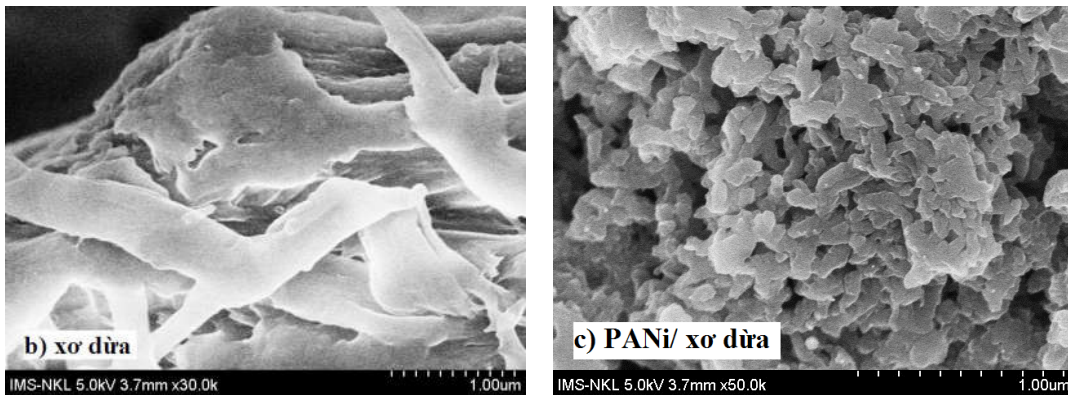
Frequency $\nu$ ( $cm^{-1}$ )					Provided the functional groups
PANi	Coir	PANi/coir	Sawdust	PANi/sawdust	
--	3419	3429	3336	3213	OH
--	2924; 1057	2953	2933	2902	C-OH
--	1653	1643	1649	1647	C=C
--	1105	1107	1051; 1029	1020	O-CH <sub>3</sub>
3431; 3302	--	3358	--	3213	N-H amine 2
3057; 2933	--	3078	--	3047	C-H benzene ring
1566	--	1560	--	1570	ring benzoid
1489	--	1481	--	1483	Quinoid diamine format
1296	--	1294	--	1292	-N=quinoid=N-
1242	--	1238	--	1238	C-N benzene of diamine
1138	--	1107	--	1151	C-N <sup>+</sup>

### 3.2.3. The results of analysis of materials by scanning electron micrographs



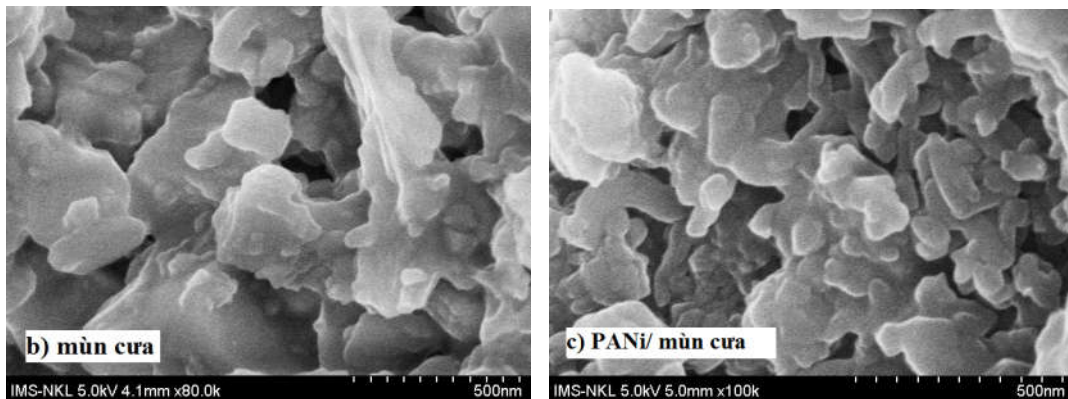
*Fig. 3.27. SEM images of original material absorbs PANi*

Photo taken with scanning electron microscope - SEM (Fig 3.27) showed absorption materials PANi synthetic origin in the form of fiber, stacked and porous nanoscale fiber diameter of about 35-50 nm, consistent and consistent with the results of the study.



*Fig. 3.30. SEM images of coir (b) and PANi/ coir (c)*

Scanning electron microscopy (SEM) (Fig. 3.30) of absorbent materials PANi/coir, showed that the coir was coarse and spongy in size and material size was within the range  $100 \div 500$  nm. Thus, PANi material is synthesized on coir (PANi/ coir) which is fibrous, overlapping and foamed with a nanometer diameter in the range of  $500 \div 600$  nm. This indicates that the PANi material was synthesized on the coir carrier.



*Fig. 3.33. SEM images of sawdust (b) and PANi/ sawdust (c)*

The scanning electron microscope image (Fig. 3.33) shows that the sawdust (Fig. 3.33.b) are crushed and have a nanometer size of about  $100 \div 300$  nm. Thus, PANi material found on sawdust (PANi / Sawdust - Fig 3.33.c) also has a filamentous, spongy shape and overlaps with a nanometer diameter of  $150 \div 300$  nm. The PANi material was synthesized on a sawdust carrier.

### **3.3. Survey DDT adsorption capacity of the original materials PANi**

To evaluate the absorption of synthetic materials have been sourced from PANi, coir, and sawdust. Within the scope of the thesis, some pesticides are chemical compounds persistent organic environmental pollutants has been selected to conduct research experiments absorbed by the material in the

original PANi various events such as absorption material changes PANi original different nature, the material of the monomer ratio with carrier Ani (coir, sawdust) changes in the synthesis PANi, change time absorption, change the volume of the material absorbed, changing the concentration of the absorbed substances (pesticides - POP).

### 3.3.1. The influence of the material nature original PANi

#### 3.3.1.2. Absorption of original materials PANi/ coir

The capacity and adsorption efficiency of DDT by PANi based materials and coconut fiber is shown in Fig. 3.37, which shows the adsorption capacity of the total DDT compounds of the high adsorption materials. In particular, unmixed adsorbents (coir, PANi, activated carbon) have poorer adsorption properties than PANi adsorbed materials (PANi/coir, PANi + coir, PANi + activated carbon). Specifically, the coconut fiber has the lowest adsorption capacity of 37.29 mg/g and the efficiency is %H = 60.29%, PANi/coir and PANi + coir have the best adsorption capacity, in which PANi material / coir has an adsorption capacity  $q = 47,65 \text{ mg / g}$ , achieving high efficiency %H = 77 %.

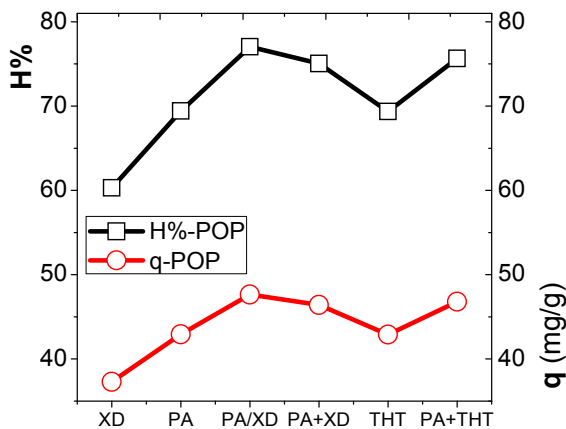


Fig. 3.37. Ability to absorb the material substance of the original POP PANi and coir

From the above analysis we can conclude the following:

- The original PANi absorption material and coir are capable of absorbing the chemical pesticide persistent organic as DDE, DDD and DDT. In particular, absorption materials with the original PANi mixed with coconut fiber as PANi/ coir, PANi+XD has the ability to absorb organic compounds better Persistent individual materials alone as coir, PANi and activated carbon. From there, it is possible to use the original form PANi absorption material modified with hybrid coconut fiber material to absorb organic compounds, persistent (organic pesticide) in the processing environment.

- In the three organic compounds are absorbed persistent with the original materials PANi and coir synthesized the compounds absorption by the material DDE is the worst and the best that DDT reaches performance  $H\% \approx 80\%$

### 3.3.1.2. Absorption of original materials PANi/ sawdust

Fig. 3.41 for the performance and absorption capacity of total organic compounds persistent - POP was high and we have laws like the original absorption materials PANi/ coir studied above. In particular, the absorption material such as sawdust, activated carbon, PANi absorption are inferior to the original materials PANi is mixed, denatured with sawdust as PANi/ sawdust, shavings of PANi. Specifically, sawdust has the ability to absorb organic compounds with the worst persistent with capacity  $q = 40.8$  mg/g performance hit  $H\% = 66\%$  and root absorption material and sawdust PANi best absorption with capacity  $q = 45.8 \rightarrow 47.9$  mg/g and  $\%H = 77.5\%$  performance reached.

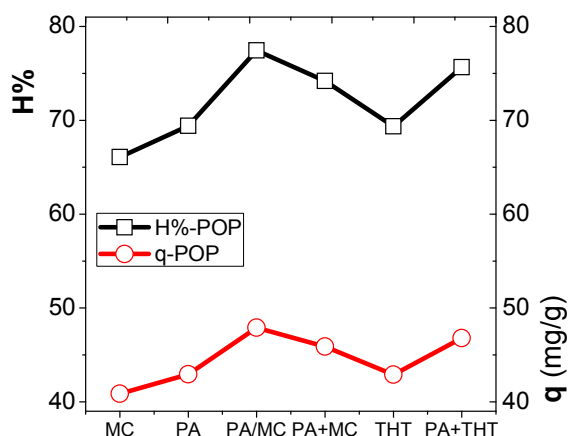


Fig 3.41. Ability to absorb the material substance of the original POP PANi and sawdust

From the above analysis we can conclude the following:

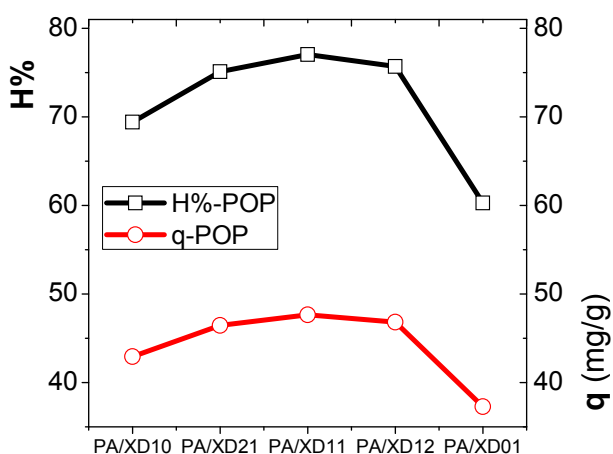
- The original PANi absorption material and sawdust have the ability to absorb organic compounds as persistent as DDE, DDD and DDT. In particular, absorption materials with the original PANi mixed with sawdust as PANi/ sawdust, PANi + sawdust with better absorption of the individual materials alone as sawdust, PANi and activated carbon. Since then, also can use the original sample absorption materials PANi hybrid modified with sawdust to absorb material compounds Persistent Organic (organic pesticide) in handling similar environment as coir above.
- In organic compounds are absorbed persistent with the original materials and sawdust PANi synthesized the compounds absorption by the material DDE is the worst and the best that DDT compounds achieve  $H = 79.5\%$  interest of PANi/sawdust materials.

### 3.3.2. The influence of monomer ratio Ani and coir, sawdust original

#### 3.3.2.1. Effects of aniline monomer ratio and initial coir

DDT-total (DDD, DDE and DDT) adsorptive efficiency and capacity of the PANi-based materials are shown in Figure 6. It is shown that the synthetic materials have a good adsorptive capacity. As for PAXD01, it has the lowest adsorptive capacity with  $q = 37.3$  mg/g and its adsorptive performance was

60.28%. Considering PAXD10, its adsorptive capacity increased in comparison to PAXD01, with  $q = 42.93$  mg/g and its efficiency was 69.4%. The max adsorptive capacity  $q$  is  $46.4 \div 47.65$  mg/g and its performance up to 77%. When the original ratio of ANi and coir was altered; that is, there was the combination PANi with coir under the synthesis process (PAXD12, PAXD11 and PAXD21 materials), the adsorptive capacity towards DDT compounds increased to about  $q = 46.4 \div 47.65$  mg/g and its performance up to 77%, which was better than without their combination.



Hình 3.45. Khả năng hấp phụ chất DDT tổng của các vật liệu gốc PANi/ xơ dừa với các tỉ lệ ban đầu monome ANi và xơ dừa

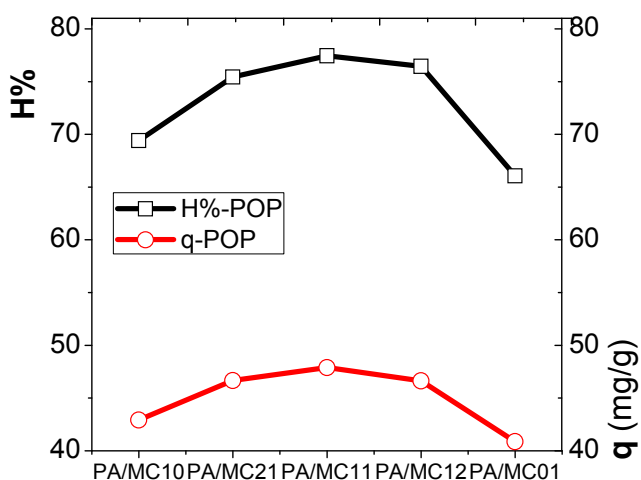
From the analysis and evaluation of the above can be concluded as follows:

- The original material absorption and coir PANi with aniline monomer ratio/ coir different initial absorption are compounds pesticide persistent organic environmental pollutants. So we can use the original materials absorb PANi/ coir to handle environmental pollution pesticide chemicals Persistent Organic by taking advantage of agricultural waste is coconut fiber combined with PANi.
- In the three organic compounds studied treatment is DDE, DDT, DDD and we see, the ability to absorb the worst DDE compound ( $q = 10.21 \rightarrow 13.75$  mg/g and  $H\% = 53.6 \rightarrow 72.2\%$ ), while the compound DDD absorption capacity but smaller absorption efficiency greater than ( $q = 7.73 \rightarrow 9.57$  mg/g and  $H\% = 61.4 \rightarrow 76\%$ ), while for the DDT compounds have the greatest absorption capacity  $q = 23.9$  mg/g and efficiency  $H\% = 79\%$ .

### 3.3.2.2. Effects of aniline monomer ratio and sawdust

Performance and capacity to absorb the total compounds have persistent - POP by the original materials PANi/ sawdust with different initial ratio of monomer aniline and sawdust in Figure 3.49, we see the material synthesized from aniline and sawdust have good absorption of chemical pesticide persistent organic from the original aqueous solution.





Hình 3.49. Khả năng hấp phụ các chất DDT tổng của các vật liệu gốc PANi/ mùn cưa với các tỉ lệ ban đầu monome ANi và mùn cưa

Similarly absorption of each compound of DDD, DDE and DDT, the compounds POP total rule also absorb the same. Specifically, divided into 2 groups, group materials PA/MC01 and PA/MC10 is capable of POP compounds absorbed poorly and original material present PANi (PA/MC10 with  $q = 43$  mg/g performance hit 69.4%) have a higher absorption capacity is not present original material PANi (PA/MC01 with  $q = 40.9$  mg/g of 66% efficiency). Next, the class of materials capable of absorbing high POP compounds (PA/MC21, PA/MC12 and PA/MC11) absorption capacity in the range of  $q = 45.9 \rightarrow 46.7$  mg/g, efficiency  $H\% = 74.2\% \rightarrow 77.53\%$ .

*From the analysis and evaluation of the above we can conclude the following:*

- The original PANi absorption material and sawdust with the original aspect ratio of monomers ANi/sawdust are also different absorption pesticide compounds persistent organic environmental pollutants - POP with good results from aqueous solutions. From there, we can use the original materials absorb PANi/sawdust to absorb the chemical pesticide persistent organic environmental pollutants in waste utilization of production facilities sawdust, wood materials combined with PANi.
- In organic compounds persistent environmental pollutants studied absorption is DDE, DDD and DDT. We see, the ability to handle DDE compound is worst performance hit in the range  $H\% = 54.9 \rightarrow 72.5\%$  with absorption capacity reaches  $q = 10.46 \rightarrow 13.8$  mg/g. Next, compounds DDD processing performance achieved  $H\% = 70.5 \rightarrow 75.53\%$  absorption capacity in the range less than of  $q = 8.7 \rightarrow 9.51$  mg/g. The compound has the highest processor performance is DDT absorption capacity is the largest  $q = 23.7$  mg/g and performance hit  $H\% = 77.53\%$ .

✓ **General conclusion**

- *From the analysis, evaluation processing capability to absorb the chemical pesticide persistent organic - POP material absorbed by the*

root PANi, coir, and sawdust were synthesized in Section 3.3.1 and Section 3.3.2, we can conclude generally as follows: In the studied sample material, they are likely to absorb the compound handle persistent organic - from the extraction solution POP contaminated soil washing drugs pesticides with high efficiency from 60.3 → 77.53% to absorption capacity POP total reach 37.3 → 47.9 mg/g.

- The original material absorbed with denatured PANi coir and sawdust can be studied for application processing aqueous solutions containing organic compounds causing environmental pollution such as chemical pesticides, sewage from the house textile dyeing machines, villages, ....
- After doing the experiments conducted to study the effects of pesticide absorption with persistent organic materials by original absorption PANi/coir and PANi/sawdust and within the framework of the thesis I chose the original absorption material PANi/coir, who's initial aniline monomer/coir = 1/2 (with  $q = 46.8$  mg/g and  $H\% = 75.7\%$ ) for the conduct of research the following effects: absorption time, the mass of absorbing material, the concentration of the substance initially absorbed (pesticides) and the model of the absorption isotherm.

### 3.3.3. Influence of time

Increased absorption time in the period from 0 → 40 minutes and the time from 40 → 160 minutes, the absorption capacity and the absorption efficiency has increased but not significantly change ( $q = 49.2 \rightarrow 50.1$  mg/g and  $H = 79.6 \rightarrow 81\%$ ), suggesting that the absorption of organic compounds are persistent in the original materials PANi/ coir have reached equilibrium. So the time to reach equilibrium absorption process is 60 minutes.

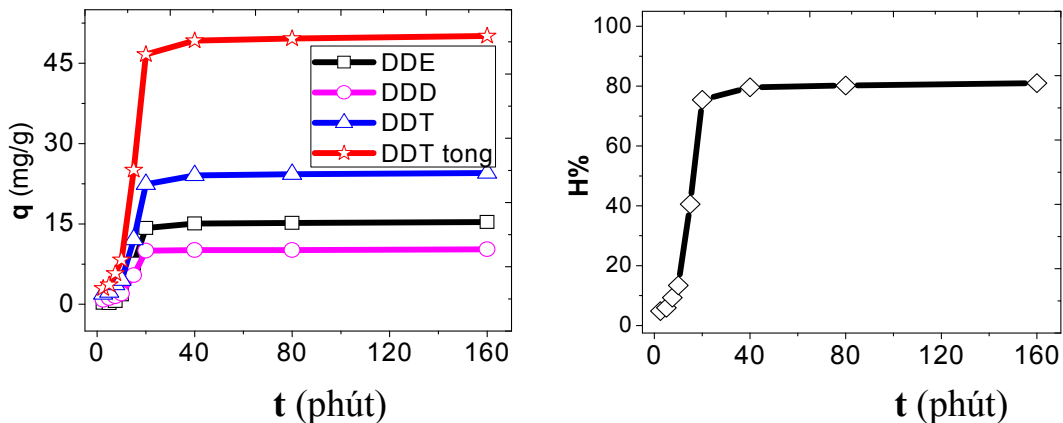


Fig 3.50. Influence of time to absorption capacity and absorption efficiency POP compounds with original materials PANi/ coir

### 3.3.4. Influence of adsorbent mass

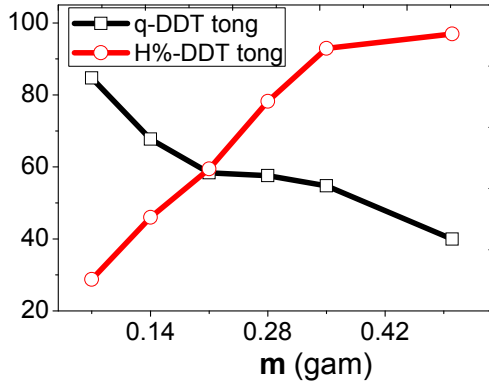


Fig 3.54. Absorption of POP substances when changing the mass of absorbing material

Performance compounds absorbed DDE, DDD, DDT is increased strongly with increasing mass of the material absorbed from 0.07 grams to 0.35 grams, while continuing to increase the volume of material from 0.35 grams to 0.5 grams absorption performance we see not only increased much from 93 → 97%, which suggests that the absorption has reached equilibrium and the continuing increase of the volume of material to absorb up the performance of the absorption will not rise much. Along with the increased efficiency of absorption, the absorption capacity was found to be inversely proportional to the absorption performance of the original materials PANi/ coir used.

### 3.3.5. Influence of initial adsorbed concentration

We see, in the range of concentrations studied surveying changes have a common rule is to increase the concentration of the original absorbed absorption capacity are increased in a linear (or absorption capacity billion proportional to the concentration of the substance is absorbed), but the absorption efficiency of the process decreases according to linear (or absorption efficiency is inversely proportional to the concentration of the substance is absorbed).

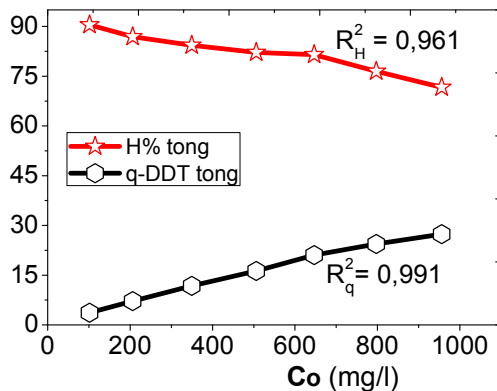


Fig. 3.60. The influence of the concentration of the original substance absorption performance and absorption capacity of the overall DDT compounds

When absorbed concentration increases, the absorption capacity tends to rise slowly in the final concentration increases, but that does not alter the relationship between the concentration of absorbed with performance and POP absorption capacity total is linear (correlation coefficient  $R^2_q = 0.961$

and  $R^2_H = .991$ ; Figure 3.89) with  $C_{01} = 101.4$  ppm (with  $q = 3.7$  mg/g and  $H\% = 90.5\%$ ) to  $C_{07} = 955.86$  ppm concentration (with  $q = 27.4$  mg/g and  $H\% = 71.7\%$ ).

### 3.4. Model absorption isothermal

#### 3.4.1. Model Langmuir isotherm

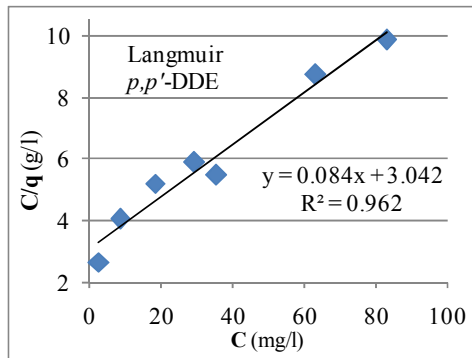


Fig. 3.61. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original material absorbs PANi / coir to  $p,p'$ -DDE

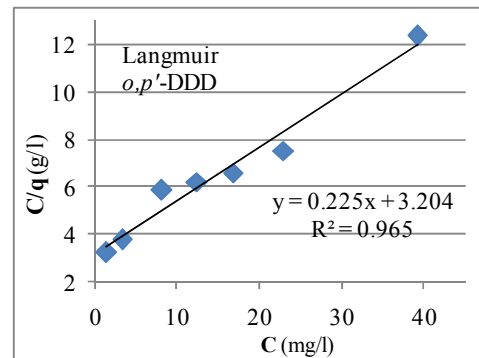


Fig. 3.63. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original material absorbs PANi / coir to  $o,p'$ -DDD

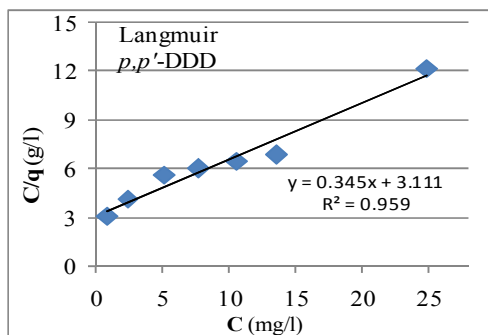


Fig. 3.65. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original material absorbs PANi/ coir to  $p, p'$ -DDD

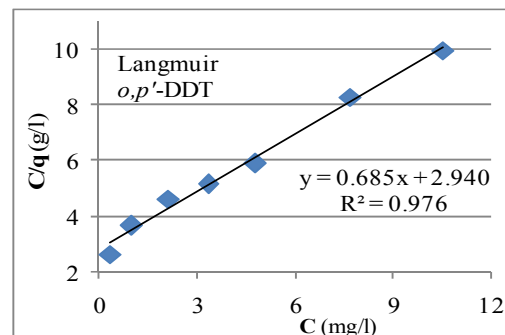


Fig. 3.67. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original material absorbs PANi/ coir to  $o,p'$ -DDT

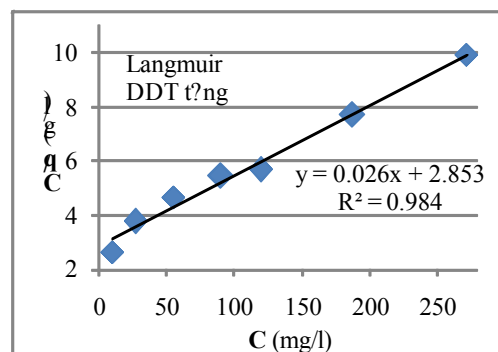
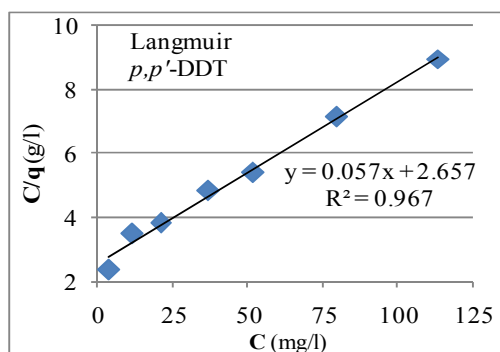


Fig. 3.69. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original material absorbs PANi/ coir to  $p,p'$ -DDT

Fig. 3.71. The relationship between  $q$  and  $C$  according to the Langmuir isotherm absorption of original materials PANi/ coir for POP total

Table 3.15. The parameters in the model Langmuir isotherm adsorption material for PANi/ coir

Compound	Linear equations	$R^2$	$K_L$ (l/mg)	$q_{max}$ (mg/g)
$p,p'$ -DDE	$y = 0.84x + 3.042$	0.962	0.0276	11.9
$o,p'$ -DDD	$y = 0.225x + 3.204$	0.965	0.07	4.45
$p,p'$ -DDD	$y = 0.345x + 3.111$	0.959	0.110	2.9
$o,p'$ -DDT	$y = 0.685x + 2.94$	0.976	0.233	1.46
$p,p'$ -DDT	$y = 0.057x + 2.657$	0.967	0.0214	17.54
POP tổng	$y = 0.026x + 2.853$	0.984	0.009	38.46

From the results of analysis and evaluation can conclude the following:

- These compounds have persistent - POP are likely to be absorbed obey Langmuir isotherm models absorbed by the original material PANi/ coir, the absorption of the fit between theory and experiment for Langmuir isotherm model.
- The correlation coefficient  $R^2$  of the model for each individual compound and overall POP are quite high, in the range of 0.959  $\rightarrow$  0.984. In particular, the pattern of the overall POP largest Conformity ( $R^2 = 0.984$ ).
- $R_L$  parameter Langmuir balance between  $0 < R_L < 1$  is favorable values for absorption model Langmuir isotherm
- The value of maximum absorption capacity  $q_{max\ DDT\ total} = 38.46$  mg/g in line with some of the above findings to the original material that absorbs other PANi.

### 3.4.2. Model Freundlich isotherm

From figure 3.73 to 3.78 is the graph Freundlich equation form:

$$\ln q = \ln K_F + 1/n \cdot \ln C$$

From there, identify the parameters related to Freundlich isotherm models and the results are presented in Table 3.16.

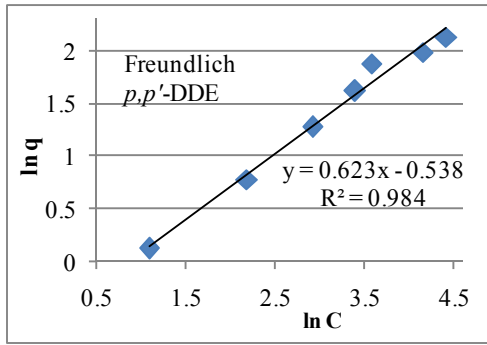


Fig. 3.73. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original material absorbs PANi / coir for substance p, p'-DDE

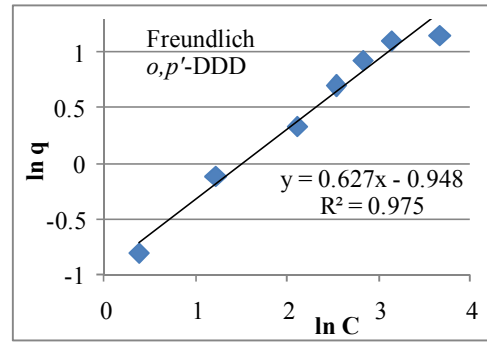


Fig. 3.74. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original material absorbs PANi / coir for substance o, p'-DDD

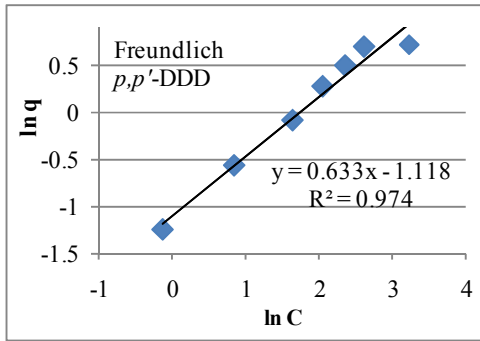


Fig. 3.75. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original material absorbs PANi / coir for substance p,p'-DDD

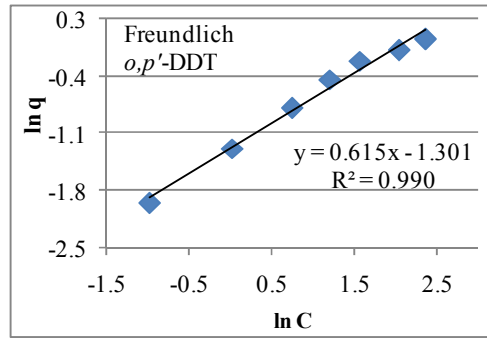


Fig. 3.76. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original material absorbs PANi / coir for substance o,p'-DDT

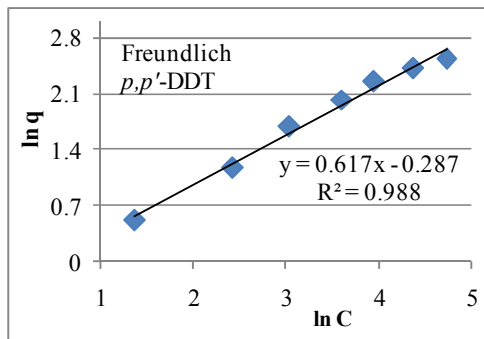


Fig 3.77. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original material absorbs PANi/ coir for substance p,p'-DDT

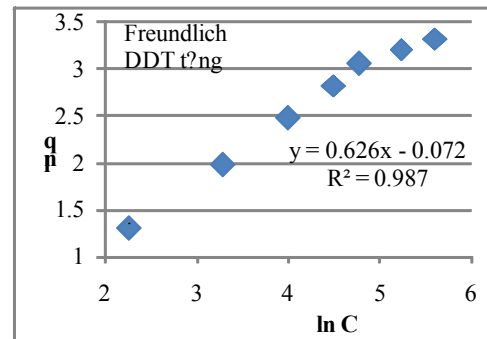


Fig 3.78. The relationship between  $q$  and  $C$  under isothermal equation Freundlich absorption of original materials PANi/ coir for POPs total

From Table 3.16 has made the following remarks:

- The value of the coefficient  $n$  in Freundlich isotherm models:  $1 < n < 10$  are all within convenient for follow Freundlich isotherm models.
- The correlation coefficient of linear regression  $R^2$  reaches high values in the range of  $0.974 \leq R^2 \leq 0.990$ , values also confirmed that the absorption obey Freundlich isotherm model. In particular, compounds *o,p'*-DDT follow best model ( $R^2 = 0.990$ ) and compound *p,p'*-DDE follow smallest model ( $R^2 = 0.974$ ). However, the  $K_F$  parameters characterizing the ability of the system to absorb the small value  $1.08 \leq K_F \leq 3.67$  (mg/ g), this means that the system is poorly adsorbed, so it is not appropriate to use the Freundlich isotherm model to evaluate the adsorption process.

*Table 3.16. The parameter values for Freundlich isotherm models*

<b>Compound</b>	<b>Linear equations</b>	<b><math>R^2</math></b>	<b><math>n</math></b>	<b><math>K_F</math></b>
<i>p,p'</i> -DDE	$y = 0.623x - 0.538$	0.984	1.605	1.71
<i>o,p'</i> -DDD	$y = 0.627x - 0.948$	0.975	1.595	2.58
<i>p,p'</i> -DDD	$y = 0.633x - 1.118$	0.974	1.580	3.06
<i>o,p'</i> -DDT	$y = 0.615x - 1.301$	0.990	1.626	3.67
<i>p,p'</i> -DDT	$y = 0.617x - 0.287$	0.988	1.621	1.33
POPs total	$y = 0.626x - 0.072$	0.987	1.598	1.08

***From the analysis, the evaluation process of absorption of the original material absorbs PANi / Coir by two Langmuir model and Freundlich isotherm can make the following conclusions:***

- The compound *p,p'*-DDE: The absorption of *p,p'*-DDE with original material absorbs PANi/coir are consistent with both the Langmuir model and Freundlich isotherm, which Langmuir isotherm model appropriate and more favorable due to coefficient  $K_F$  Freundlich small. From there, determine the maximum absorption capacity of *p, p'*-DDE material PANi/coir  $q_{max} = 11.9$  mg/g and value  $K_L = 0.0276$  l/mg range favorable for absorption.
- Compound *o,p'*-DDD: The absorption of *o,p'*-DDD with original materials PANi/ coir have a correlation coefficient of linear regression  $R^2 = 0.965$  for high-model and Langmuir isotherm  $R^2 = 0.975$  for Freundlich isotherm model, demonstrates both fit both models, but after analyzing the kinematic parameters that the model Langmuir Freundlich model better suited to the absorption capacity  $q_{max} = 4.45$  mg / g and constant  $K_L = 0.07$  l/mg.
- The compound *p,p'*-DDD: The same *o,p'*-DDD, the compound *p,p'*-DDD high correlation coefficient  $R^2 = 0.959$  for the Langmuir isotherm models and  $R^2 = 0.974$  for Freundlich isotherm model. Models Langmuir

Freundlich model better suited for absorption capacity  $q_{\max} = 2.9$  mg/g and constants  $K_L = 0.110$  l/mg.

- Compound o,p'-DDT: The absorption of o,p'-DDT with original materials PANi/ coir follow Langmuir isotherm model with  $R^2 = 0.976$  and Freundlich isotherm model with  $R^2 = 0.990$ . In particular, the Langmuir model is more suitable than the Freundlich model and the maximum adsorption capacity for o, p'-DDT is  $q_{\max} = 1.46$  mg/g and constant  $K_L = 0.233$  l/mg.
- The compound p,p'-DDT: The absorption of o,p'-DDT with original materials PANi/ coir follow Langmuir isotherm model with  $R^2 = 0.967$  and Freundlich isotherm model with  $R^2 = 0.988$ . In particular, the Langmuir model is more suitable than the Freundlich model with more reasonable parameters, the adsorption capacity for o, p'-DDT is  $q_{\max} = 17.54$  mg/g and constant  $K_L = 0.0214$  l/mg.
- DDT-total compounds: As a combination of the above compounds should be considered separately for both the absorption of organic compounds Persistent original POP materials PANi/ coir follow two models Langmuir isotherm ( $R^2 = 0.984$ ) and Freundlich ( $R^2 = 0.987$  have), review the whole process between theory and experiment show Langmuir model is more suitable for maximal adsorption capacity  $q_{\max} = 38.46$  mg/g and constant  $K_L = 0.009$  l/ mg.

**General conclusion:** The adsorption process of the DDT, DDD, DDE compounds from PANi/ coir composite materials is more suitable for the Langmuir isothermal model, thus it can be concluded that these compounds are adsorbed on a surface of adsorbent material with uniform structure. This means that the components of DDT, DDD, DDE are adsorbed by homogeneous concentricity on the surface of PANi/ coir and the process is monolayer adsorption.

### 3.5. The next direction of decomposition of DDT compounds

After studying the treatment of DDT, DDD, DDE compounds extracted from the soil by PANi conductive polymer materials, the amount of DDT compounds collected has been retained in PANi materials, there are two directions to thoroughly research DDT:

1. PANi materials containing DDT compounds will be decomposed by burning, this method will cost very little money because the processing weight is very small from few grams to several dozen grams of PANi material compared to having to transport tons of contaminated land to cement plants for burning, it would be costly.



2. The compounds of DDT will be dissolved with suitable solvents and then decomposed by chemical methods and electrochemicals in the electrolysis system ( $C_2H_5OH + CaCl_2$ ) into non-toxic compounds that do not pollute the environment. (Works 5 and 7 in the list of published scientific works, page 126).

## CONCLUDE

1. Solvent systems QH1, QH2, QH3 are capable of extraction and purification of plant protection chemicals, DDT 63,68%, DDD 31,11%, DDE 4,31% from contaminated soil with the efficiency of total three successive extractions of solvents are very high. Specifically, the QH1 solvent system reaches 96.2%, the solvent system QH2 reaches 97.5% and the solvent system QH3 reaches 98% even at the low level of 15%. This shows that the extraction of DDT contaminated soil with the three solvent systems can be used to clean the contaminated soil environment.
2. Synthesized 07 electrically conductive polymer material PANi original, including 06 material handling hybrid modified with coir and sawdust by chemical polymerization method with the ratio of the initial volume aniline monomer and coir or sawdust with different proportions 1/2, 1/1, 2/1 high efficiency from 83.2 → 92%. The synthetic material has been analyzed their characteristics methods by infrared spectroscopy (IR) and scanning electron micrographs (SEM), The result confirmed that PANi was formed on coir and sawdust in the form of nanometers.
3. The results of studying the adsorption process of DDT, DDD and DDE compounds in the extracts of the synthesized materials show that, although they were synthesized under other conditions of the initial mass fraction ratio of Aniline monomers with coir or sawdust (1/2, 1/1, 2/1) but capable of adsorbing DDT, DDD, DDE compounds with high efficiency of 60.3 ÷ 77, 53%.
4. Determine the adsorption capacity of the material, in which the total DDT adsorption capacity corresponding to the PANi material is  $q = 42.93$  mg/g, PANi/sawdust material with an ANi/sawdust ratio of 2/1, 1/1, 1/2 had an absorption capacity of 46.66; 47,89; 46.63 mg/g, PANi/ coir material with an ANi/ coir ratio of 2/1, 1/1, 1/2 with an adsorption capacity of 46.45; 47,64; 46.82 mg/g. In particular, PANi materials are synthesized on sawdust and coir which have better DDT adsorption capacity than individual materials or mechanically mixed together.

5. Have identified the time to reach adsorption equilibrium DDT compounds in the root conductive polymer materials PANi/ coir is the time from 40 ÷ 60 minutes.
6. Adsorption DDT from extracts comply with the Langmuir isotherm model parameter Langmuir balance  $0 < R_L < 1$ , For the Freundlich model, the  $K_F$  characteristic for the adsorption capacity of the system is small at  $1.08 \leq K_F \leq 3.67$  (mg/g). This shows that the Langmuir isothermal model is more suitable than the Freundlich isothermal model.

**Recommendations:** More in-depth studies of DDT extraction from soil and adsorption of DDT by PANi base materials on mechanics, thermodynamics, ... from there to clarify the absorption capacity of the PANi material for DDT.

### NEW POINTS OF THESIS

1. Researched handling compounds extracted DDT, DDD, DDE from contaminated soil using organic solvent systems QH1, QH2, QH3 with high performance. from there, opening a new direction in handling the pollution hotspots of pesticides - DDT by extraction with solvent wash original linear alcohol environmentally friendly, alternative technology uncertain and expensive burning as it is today.
2. Synthetic PANi polymer-based polymer materials are synthesized on the carrier material such as coir and sawdust in various conditions, nanometer size and these materials are used to adsorb organic pollutants such as DDT, DDD, DDE to extract contaminated soil, reaching adsorption capacity of over 45 mg/g.
3. Results analysis shows, there appears the transformation of DDT to DDD during extraction with the solvent QH is from 2.00 ÷ 58.89%. The new point is that there identified with the transformation in the extraction wash pesticides and quantify metabolic rate.
4. From the results of applied research Langmuir isotherm models and Freundlich isotherm models material for PANi / coir and PANi / sawdust for compounds DDT, DDD, DDE shows the Langmuir isotherm model fit the experimental than Freundlich isotherm model.

## SCIENCE WORKS HAS PUBLISHED

1. **Nguyen Quang Hop**, Le Thi Thuy Duong, Phan Thi Ngat, Duong Quang Huan, Nguyen Van Bang and Le Xuan Que (2013), *Studying a separation of persistent insecticide residues in soil using water extraction with additive QH1*, Journal of Chemistry, Vol. 51 (6ABC), 445-448.
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8. **Nguyen Quang Hop**, Le Xuan Que (2017), *Study synthesis of PANi/ coir material for adsorption of DDT in contaminated soil extraction*, Vietnam Journal of Chemistry, Vol. 55 (5).

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1. 6th National Chemistry Conference, Hanoi, 2013.
2. Young Scientist Science Conference of the National University of Education the fourth time, Hai Phong, 2014.
3. Journées Scientifiques Franco-Vietnamiennes de “Chimie et Matériaux Avancés pour l’Environnement” - CMAE 2015 – Hanoi, in Faculty of Chemistry - Hanoi University of Science - VNU.
4. Young Science Conference of Hanoi Pedagogical University No.2 in years 2014 and 2016.
5. The Polymer Science Specialist Conference 2016 - Polymer chemistry, in Institute of Tropical Techniques - Vietnam Academy of Science and Technology.