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Study on synthesis of PANi/coir material for adsorption of DDT in contaminated soil extracts

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Abstract

The efficiency of synthesized polyaniline (PANi) with the presence of coir in sulfuric acid medium and ammonium persulfate as oxidizing agent varies from 83.20 to 92.00 %. The obtained polyaniline/coir material was used for adsorption of dichloro diphenyl trichloroethane (DDT) - a pesticide which has been used and still causing serious pollution problems. The adsorbent efficiency is 77.00 % corresponding to adsorptive capacity 47.65 mg/g at room temperature.

Keywords. Polyaniline, coir, DDT, adsorption, pesticide.

1. INTRODUCTION

The environment pollution is currently causing many negative issues to the society and also causes significant impact on human life, including the risky contamination from persistently organic pesticides. According to the Ministry of Natural Resources & Environment of Vietnam, there are over 1556 areas (villages, communes, etc.) polluted with the pesticides all over the country, especially in provinces such as Thanh Hoa, Nghe An, Ha Tinh. There is a fact that the pollution causes serious health problems, notably cancers leading the death to the local people. Hence, those contaminated areas should be immediately treated and reverted [1].

The washing and extraction method are effective and applicable to high-level pollution [2]. After extracting and washing process, the pesticides in the obtained solution need to be removed by the adsorption recovery method. Some severely contaminated areas have been isolated, and the rain water drained out is collected and treated by activated carbon [1].

However, there are many types of materials as the absorbents of high efficiency, low cost, consistency, and easy manufacturing with high durability such as conductive polyaniline materials (PANi) [3, 4] which are capable of treating heavy metals and especially persistently organic compounds like DDT, PCB. The typical PANi materials are 3 components composites prepared from PANi, coir and sawdust [5-8]. Therefore, we have conducted a research on the synthesis of PANi -based materials from aniline on coconut fiber carriers for adsorption and treatment of persistently organic chemical pesticides extracted from contaminated soil.

In this paper, the synthesis of PANi-based materials on the coir substrate as adsorbents is studied. The obtained materials are then pretreated before adsorbing DDT from the solution. Some characteristics of the prepared materials and DDT adsorption properties are also presented.

2. EXPERIMENTAL

2.1. Chemicals and equipment

The chemicals used for the experiments consisted of pure aniline (ANI), sulfuric acid, ammonium persulfate (APS), distilled water, acetone, coir, the solution containing DDT extracted from the contaminated soil.

Some necessary laboratory instruments such as magnetic stirrer, desiccator, filter paper, vacuum, funnel Buchner, pH paper, analytic scale, pipette, graduated cylinder, gloves, gas masks, labor protection clothing.

Devices for analyzing experimental results were Gas Chromatography Mass Spectrometry (GCMS) - Shimadzu (Japan) of Institute of Environmental Technology - VAST; Scanning Electron Microscope

Hitachi - S4800 (Japan) of Institute of Materials Science - VAST; FTIR Affinity - 1S- Shimadzu (Japan) of Faculty of Chemistry, University of Science, VNU.

2.2. Experiment

2.2.1. DDT sample solution

The DDT sample solution was additive - water extract of the contaminated soil collected in Hon Tro village, Dien Chau district, Nghe An province. DDT (DDT-total) in this study combines 3 components dichloro diphenyl trichloroethane (DDT), dichloro diphenyl dichloroethane (DDD), dichloro diphenyl dichloroethylene (DDE).The result of the extraction study was published [2].

2.2.2. The synthesis procedure of PANi-based materials

The coir was crushed, washed and dried.

The *PANi-based* materials were prepared in sulfuric acid (H_2SO_4) with weight ratio Ani/ coir = 1/0; 2/1; 1/1; 1/2 with ammonium persulfate as the oxidizing agent. The reaction was carried out for 15 hours at a temperature between 0÷5 °C on the magnetic stirrer.

After the experiment, PANi-based materrials were then washed several times with distilled water at neutral pH and further washed with the acetone solution to remove all the Ani residues. Finally, the materials were dried at 70 °C in a dryer. PANi's weight and synthesis efficiency were then determined. The product was stored in a sealed plastic box in a desiccator [9].

The obtained materials are labeled with the weight ratio ANi/coir by PAXD10, PAXD21, PAXD11 PAXD12 and only coir PAXD01.

The five materials were used to test adsorbing DDT in the extract with an initial concentration C_0 = 1560 ppm (mg/L) within 12 hours.

2.2.3. Experimental method

Synthetic efficiency was calculated using the formula (1):

$$\% E = \frac{m_1 - m_2}{m_3} 100\% \qquad (1)$$

Where: m_1, m_2 and m_3 are respectively the weight of PANi/ coir, coir and ANi.

Results of GCMS analysis show that the substances in the initial standard sample and after adsorption were mainly DDT, DDD and DDE. The adsorptive capacity (q) was calculated with the following formula (2):

$$q = \frac{(C_0 - C)V}{m} \qquad (2)$$

Where: **V** is the total volume of solution (L); **m** is the mass/ weight of adsorbent (g); $\mathbf{C_0}$ is the initial concentration of DDT in solution (mg/L), **C** is the concentration of DDT in solution after the test (mg/L).

3. RESULTS AND DISCUSSION

3.1. PANi/coir synthesis and characteristics

3.1.1. Synthetic efficiency

Basing on the experimental results and formula (1), the synthesis efficiency as follows: PAXD10 92.00 %, PAXD12 83.20 %, PAXD11 86.00 % and PAXD21 89.90 %.

3.1.2. Analysis of the infrared spectroscopy

The typical infrared spectroscopy *(*IR) spectra of the samples was shown in figure 1.

In figure 1a), there are oscillations of PANi's typical aromatic rings such as benzenoid round at 1566 cm^{-1} and the quinonoid in the diamine form at 1489 cm^{-1}; the valence oscillation of N-H group amine 2 at 3424 cm^{-1} and 3302 cm^{-1}, the oscillation of the benzene ring at C-H group at 3057 cm^{-1} and 2933 cm^{-1}, the oscillation of nitrogen atom double bonding with the quinonoid ring (N=quinoid=N) at 1296 cm^{-1}, the bond of carbon atom in the aromatic ring with the nitrogen atom in the diamine form at 1242 cm^{-1} and the valence oscillation of $C-N^+$ group at 1138 cm^{-1}.

In the figure 1b), the typical oscillation of coir structure, whose main component is cellulose, is at 3419 and OH group at 3332 cm^{-1}, the C-OH group oscillation at 2924 and 1056 cm^{-1}, the oscillation of C = C group at 1653 cm^{-1}, the valence oscillation of lignin $O-CH_3$ group at 1056 and 1035 cm^{-1}.

Similarly, the figure 1c) also shows signals of functional groups characterizing PANi such as the benzoid ring at 1560 cm^{-1} and quinoid ring in form of diamine at 1481 cm^{-1}, the valence oscillations of N-H groups amine 2 at 3429 cm^{-1} and 3358 cm^{-1}, the oscillations of C-H group in the benzene ring at 3078 cm^{-1}, the oscillation of nitrogen atom double bonding with the quinoid ring (N=quinoid=N) at 1294 cm^{-1}, the bond of carbon atom in the aromatic ring with the nitrogen atom in the diamine form at 1238 cm^{-1} and the valence oscillation of $C-N^+$ group at 1107 cm^{-1}. Also, there was a sign of typical functional groups of cellulose in the infrared spectrum of PANi/coir: oscillation of OH group at 3429 cm^{-1}, oscillation of C-OH group at 2953 cm^{-1} and oscillation of the double bond C=C at 1643 cm^{-1}.

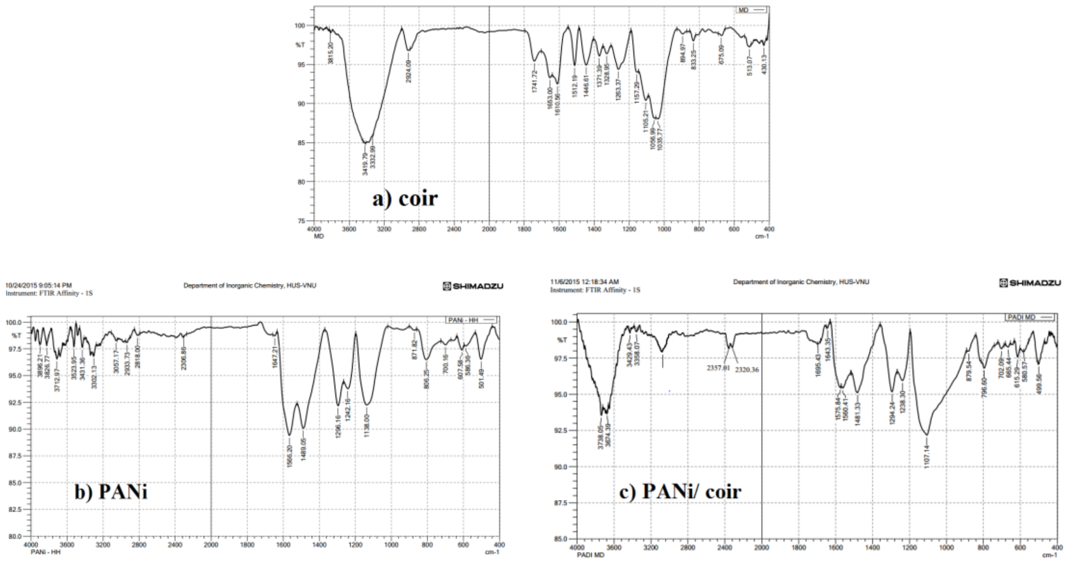

Figure 1: The infrared spectra of coir (a), PANi (b) and PANi/coir (c)

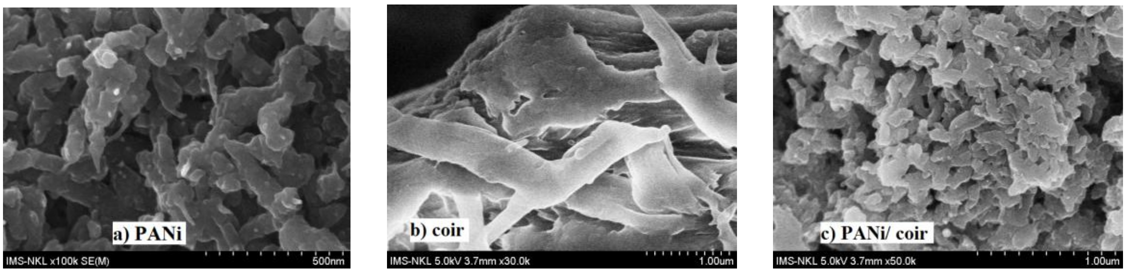

Figure 2: SEM image of PANi (a), coir (b) and PANi/coir (c)

3.1.3. SEM images

The SEM images (Fig. 2) of PANi shows that PANi is in fibrous and porous form and stacked with the fiber diameter of 35-50 nm. The milled coir formed a long and porous fiber with the size ranging from 100-500 nm. Thus, the PANi based/ coir (PAXD) material was also fibrous, porous stacked with the dimension in the range of 150-600 nm. Clearly, PANi was synthesized on the coir substrate.

3.2. Adsorptive capacity with DDT compounds

3.2.1. DDE compound

These PANi-based materials synthesized with different initial proportions of Ani monomer and coir had different adsorptive capacities with DDE compounds (Fig. 3). In particular, the absorptive capacity of only coir (PAXD01) with DDE was the lowest, reached only q = 10.2 mg/g, followed by only PANi (PAXD10) with q = 11.26 mg/g. Meanwhile, the materials of PANi with coir (PAXD21, PAXD11, PAXD12) has better adsorptive capacities of DDE compound with q = 10.21÷14.15 mg/g.

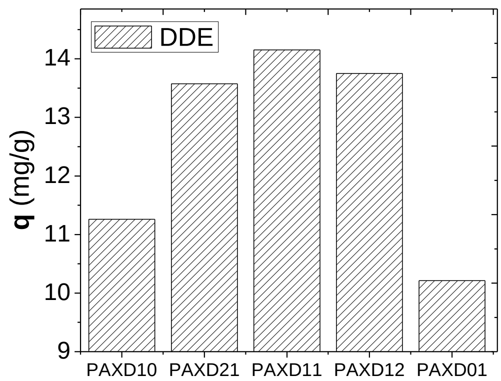

Figure 3: Adsorptive capacity of DDE compound

3.2.2. DDD compound

The DDD adsorptive capacity of the PANi-based materials q is in the range of 7.73÷9.59 mg/g, and the absorptive capacity tends to increase with the increase in ANi and tends to decrease when coir portion rises (figure 4). So, when ANi and coir were combined, the absorption of DDD was better than the in independent use.

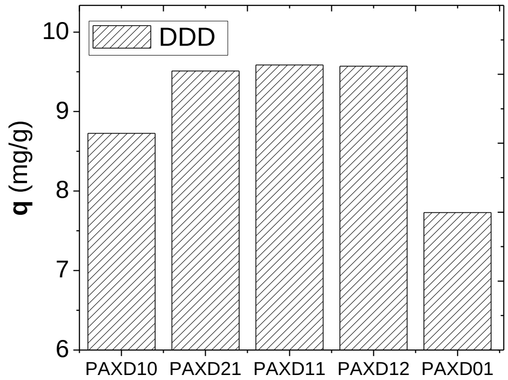

Figure 4: Adsorptive capacity of DDD compound

3.2.3. DDT compound

DDT adsorptive capacity (figure 5) was quite high and about twice to three times higher than DDE and DDD. With DDT, only PAXD01 (with q = 19.3 mg/g) has less adsorptive capacity than the other four materials (with q = 23÷23.9 mg/ g). This also proves that the PANi-based materials have a better adsorptive capacity for DDT than DDE and DDD.

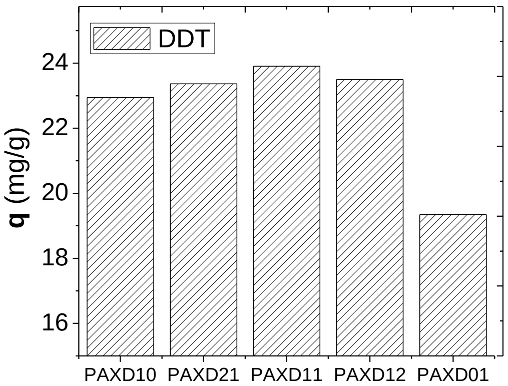

Figure 5: Adsorptive capacity of DDT compound

3.2.4. Adsorptive capacity of DDT-total

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÷47.65 mg/g and its performance up to 77 %.

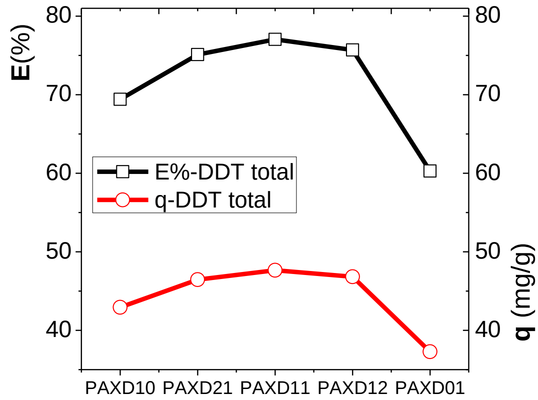

Figure 6: Efficiency and adsorptive capacity of DDT-total

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÷47.65 mg/g and its performance up to 77 %, which was better than withour their combination.

4. CONCLUSIONS

The PANi/coir adsorbents chemically synthesized with different ratios in aniline's weight were able to adsorb DDT extracted from contaminated soil. That leads to the chance of using coir in combination with PANi for adsorbing persistent organic pesticides.

The co-existent DDT's derivatives were DDE and DDD. The DDD adsorptive capacity is the lowest with q_{max} = 9.58 mg/g, followed by the DDE with q_{max} = 14.15 mg/g and DDT is the highest with q_{max} = 23.90 mg/g. Among these manufactured PANi materials, PAXD11 have the highest adsorptive capacity (47.6 mg/g) and its efficiency reaches 77.03 %.

The obtained results show that the PANi-based materials synthesized on coir substrate is capable of handling pollution problems caused by DDT and probably other POP pollutants in soil.

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