EVALUATING ABILITY OF APPLYING VIETNAMESE WOOD-BASED ACTIVATED CARBON IN PCDDs/PCDFs ANALYSIS

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Introduction

In the analytical process, activated carbon is used to enrich and separate congeners PCDDs/PCDFs from sample matrix. Some activated carbons such as AX21, Amoco PX21, Carpopak C, Carbochrom, Carboxen, Carbosphere, Norit, FAS-MD… were investigated or recommended for applying in analysis. In order to increase adsorption ability, mixing activated carbon with pulverized silica gel, celite or glass wool. Depending on the quality and quantity of activated carbon, an exact volume of appropriate solvent or solvents' mixture must be used to desorb PCDDs/PCDFs. The criterion to assess applying ability of activated carbon in dioxins/furans analysis are: not generating any interferences, separating all congeners PCDDs/PCDFs from sample matrix and desorbing at least 80% of adsorbed congeners[1,2]. With the desire of selecting Vietnamese activated carbon to apply in analysis method to replace expensive imported activated carbons, we have researched PCDDs/PCDFs adsorption on the column containing the wood-based activated carbon (namely H2). H2 is able to adsorb over 99.5% of congeners PCDDs/PCDFs from extract solution, similar to super activated carbon AX21. Over 90.9% and 92.5% of congeners PCDDs/PCDFs were desorbed from AX21 and H2 activated carbon columns only with the minimum volume of 5 ml hot toluene. Using small activated carbon column will save time, reducing chemical consume and waste in sample analysis. H2 completely met the requirements of activated carbon used in dioxins/furans analysis according to standard methods.

Materials and methods

Preparation of activated carbon columns
The wood-based activated carbon H2 (Vietnam) is pulverized, selected particle size below 0.074 mm. The super activated carbon AX21 (Anderson Development Company) in fine powder is available ground by the producer. Mixing 1 g of each activated carbon with 9 g celite 545 (ratio 1 : 9 w/w). Loading 200 mg mixture of activated carbon-celite into a glass column (4 mm inner diameter, 10 cm length), the height of adsorption material layer is 5 cm. Each end of column is fixed by 10 layers of Whatman GF/F filter. Before experiment, column is washed by 10 ml toluene, 10 ml hexane in order to remove interferences.

Preparation of PCDDs/PCDFs solutions
- Standards spiking (signed M1): Adding equal quantities of 0.5 ml solutions of isotope-labeled internal standards $^{13}C_{12}$-PCDDs/PCDFs (20-40 ng/ml) and clean-up standard $^{37}Cl_4$-2,3,7,8-TCDD (10 ng/ml) into 100 ml mixture of hexane-acetone (ratio 1 : 1 v/v). This amount of standards is equal to the amount added to each analytical sample.

- Matrix spiking (signed M3): Adding 0.1-10 g of pork fat into solution M1 to produce matrix of foodstuff sample.

- Representative "real" sample: The extracts of soil (M4), sediment (M5) and fish (M6) sampling from dioxin heavily-contaminated areas were used in this research. These solutions have specific PCDDs/PCDFs concentration of dioxin pollution in hot spots where the US army stored herbicides during the Ranch Hand operation (1962-1971).

Experimental
Each solution M1, M3, M4, M5, M6 is pressed through columns containing H2-celite and AX21-celite with flow of 1-1.5 ml/min at room temperature. Collecting the solution after flowing through column to determine escape amount

of congeners PCDDs/PCDFs. Reversing the columns, using hot toluene which is heated at 118 ±1ºC to desorb PCDDs/PCDFs by the inverted direction. The flow also is 1-1.5 ml/minute, getting fractions of each 5 ml. Adding 0.5 ml of isotope-labeled standards $^{13}C_{12}$-PCDDs (20 ng/ml) into each fraction to calculate recovery efficiency. Quantify congeners PCDDs/PCDFs by GC/MS[2]. Comparing amount of PCDDs/PCDFs which was adsorbed and escaped on each activated carbon column will evaluate adsorption efficiency as well as separation ability of congeners PCDDs/PCDFs from sample matrix.

Results and discussion

Figures 1 (a, b) are the shape image and scanning electron micrograph magnified 1000 times of the external structure of activated carbon H2.

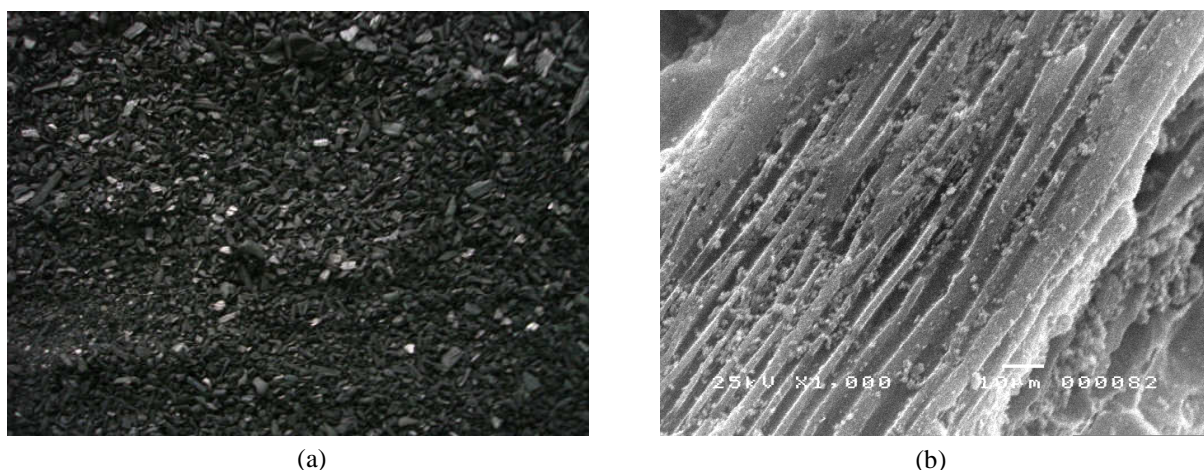(a)   (b)

Figure 1: Shape image (a) and scanning electron micrograph magnified 1000 times (b) of activated carbon H2

Research of PCDDs/PCDFs adsorption equilibrium and kinetics from solution on activated carbons AX21 and H2 estimated adsorption ability, velocity and efficiency. The results were presented in previous reports[3,4]. This research in order to assess ability and efficiency of PCDDs/PCDFs adsorption on the columns containing activated carbons AX21, H2 for analytical purpose. AX21 is used as comparable activated carbon. Adsorption efficiency is percent recovery of internal and clean-up standards which were added in samples. The result is mentioned in tables 1 and 2. In there, F0 is percent ratio of PCDDs/PCDFs found in solution after was pressed through column, corresponding with the amount of PCDDs/PCDFs escaped from column. F1 and F2 are recoveries of PCDDs/PCDFs in the first and second fractions of each 5 ml hot toluene used to desorb PCDDs/PCDFs. Symbol less than (<) indicates that congener was not found because its concentration is lower detection limit of method.

Table 1: Percent recoveries of isotope-labeled standards found in each fraction of sample M1

Activated carbon	AX21			H2		
Fraction	F0	F1	F2	F0	F1	F2
^{13}C-TCDF	< 0.5	90.9	< 0.2	< 0.2	93.7	< 0.3
^{13}C-TCDD	< 0.3	91.8	< 0.4	< 0.6	92.5	< 0.3
^{37}Cl-TCDD	< 0.3	96.9	< 0.2	< 0.2	96.1	< 0.2
^{13}C-HxCDD	< 0.4	110.2	< 0.7	< 0.7	104.1	< 0.5
^{13}C-HpCDD	< 0.5	100.0	1.6	< 0.5	99.3	1.2
^{13}C-OCDD	< 0.6	94.4	3.7	< 0.7	97.5	1.3

Table 2: Percent recoveries of isotope-labeled standards found in each fraction of matrix spiking sample M3

Activated carbon	AX21			H2		
Fraction	F0	F1	F2	F0	F1	F2
^{13}C-TCDF	< 0.2	101.7	< 0.3	< 0.3	99.7	< 0.4
^{13}C-TCDD	< 0.6	102.5	< 0.3	< 0.2	99.3	< 0.7
^{37}Cl-TCDD	< 0.2	106.0	< 0.2	< 0.7	101.8	< 0.3
^{13}C-HxCDD	< 0.7	104.1	< 0.5	< 0.5	102.1	< 0.5
^{13}C-HpCDD	< 0.5	97.3	2.0	< 0.4	97.9	1.9
^{13}C-OCDD	< 0.7	91.5	4.0	< 0.6	95.7	3.8

Tables 1, 2 show that in experimental condition PCDDs/PCDFs were not found in fraction F0, i.e. only insignificant amount (< 0,7%) of PCDDs/PCDFs in M1 and M3 samples escaped from columns. Most of congeners PCDDs/PCDFs, over 90.9% with AX21 and 92.5% with H2, are desorbed in the first fraction of 5 ml hot toluene. The rest, below 4% of PCDDs/PCDFs with AX21 and below 3.8% with H2, are desorbed in the second fraction of 5 ml hot toluene. In next fractions were not found PCDDs/PCDFs. Therefore, both columns AX21 and H2 meet with the requirements of activated carbon used in dioxins/furans analysis according to the standard BS EN 1948-2: 2006[1] and the method US.EPA8290[2]. Comparing with activated carbon AX21, which was used for years in analysis, H2 has similar adsorption ability and can very fast desorb PCDDs/PCDFs with only 5 ml hot toluene. With such a minimum volume of toluene, it reduces approximately 15-35 ml (in proportion to 75-87.5%) and even 75-95 ml (93.7-95%) to compare with the necessary volume of toluene according to standard methods.

The percent recovery of isotope-labeled standards in soil, sediment and fish samples in the first fraction of 5 ml hot toluene (F1) displayed in table 3.

Table 3: Percent recovery of isotope-labeled standards in samples M4, M5 and M6

Sample matrix	Soil M4		Sediment M5		Fish M6	
Activated carbon	AX21	H2	AX21	H2	AX21	H2
^{13}C-TCDF	104.9	89.1	90.9	90.6	78.4	79.7
^{13}C-TCDD	105.3	89.6	91.0	89.0	76.0	79.3
^{37}Cl-TCDD	113.3	91.5	102.0	91.3	89.4	91.8
^{13}C-HxCDD	105.9	92.3	90.0	82.2	88.5	92.1
^{13}C-HpCDD	89.9	87.4	83.7	86.9	81.2	79.5
^{13}C-OCDD	89.6	85.1	73.0	75.8	78.1	78.6

Tables 1, 2 and 3 show that recovery efficiency of isotope-labeled standards in samples with both activated carbons are relatively high. The percent recovery with AX21 achieved from 73.0% to 113.3%, with H2 achieved 75.8-104.1%. They are in around 40-130% which is necessary requirement to obtain in analysis methods[2,5-8]. Thus, by the use of AX21 and H2 columns, which are above prepared, will well apply to separate PCDDs/PCDFs from sample matrix as well as enriching them.

Applying ability of activated carbon H2 in analysis is showed by comparing concentration of 17 congeners 2,3,7,8-substituted PCDDs/PCDFs and total TEQ$_{PCDDs/PCDFs}$ found in samples M4, M5 and M6 with activated carbon AX21. The result is illustrated in figures 2 (a, b, c), their concentration in each sample are quite similar. The total TEQ$_{PCDDs/PCDFs}$ of each sample for both AX21 and H2 insignificantly differed, the relative standard deviation is below 4.2%. The analytical results of 30 samples, which received from International Intercalibration Studies (Sweden) and the United Nation Environment Program, with application of activated carbon AX21 and also initial use of H2 are satisfied. All samples have z-scores always < 2 and often < 1[9-13].
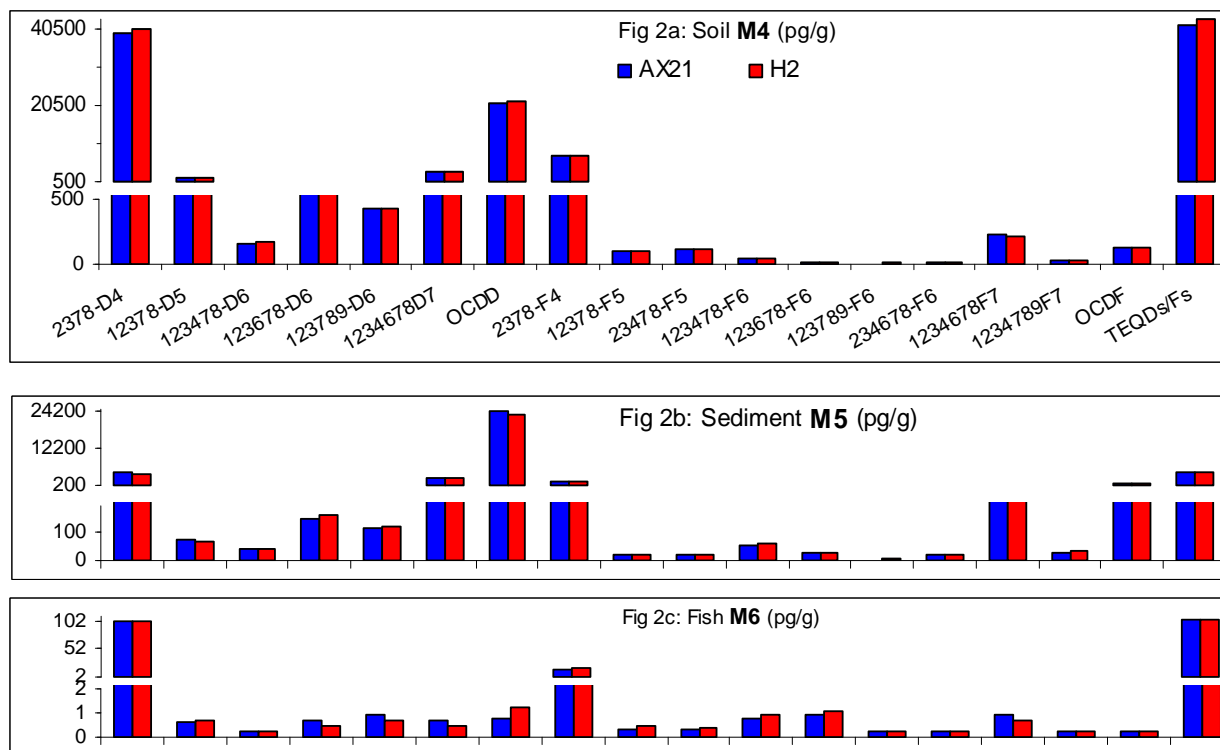
Figure 2: Comparing concentration of 2,3,7,8-substituted PCDDs/PCDFs in samples M4, M5, M6 between AX21 and H2

References
1. British-Adopted European Standard BS EN 1948-2: 2006, British Standards Institution.
2. Method 8290. US. Environmental Protection Agency, 1994.
3. Sau T.K, Truong N.X, Hung L.B, Khue D.N, Hien L.M (2009); *Organohalogen Compounds* 71: 68-73.
4. Sau T.K, Truong N.X, Dung N.T, Thu N.T, Khue D.N, Net N.X (2009); *Organohalogen Compounds* 71: 74-78.
5. British-Adopted European Standard BS EN 1948-2: 1996, British Standards Institution.
6. UNEP (2007), *Guidance for analysis of Persistent Organic Pollutants (POPs)*, UNEP Chemicals Branch, DTIE, Geneva, Switzerland, http://www.chem. unep.ch/pops/ laboratory/analytical_guidance_en.pdf.
7. Method 1613. US. Environmental Protection Agency, 1994.
8. Method 8280A. US. Environmental Protection Agency, 1996.
9. Van Bavel B, Lindström G, De Boer J and Fiedler F (2007); *Organohalogen Compounds* 69: 1285-1288.
10. UNEP (2008), *Assessment of existing capacity and capacity building needs to analyze persistent organic pollutants (POPs) in developing countries*, Final Report, United Nations Environment Programme.
11. Bert van Bavel; *Final Report 12th Round of the International Intercalibration Study*, December 2007.
12. Bert van Bavel; *Final Report 13th Round of the International Intercalibration Study*, December 2008.
13. Stefan van Leeuwen, Eirik Steindal, Bert van Bavel, Gunilla Lindstrom, Jacob de Boer; *First Worldwide UNEP Intercalibration Study on Persistent Organic Pollutants*, Report 23 February 2010.