THE EFFECT OF PCDDs/PCDFs ADSORPTION FROM SOLUTION ON ACTIVATED CARBONS - ADSORPTION ISOTHERMS RESEARCH

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Introduction

The dioxin residual levels in hotspot areas in Vietnam is many times higher than the international acceptable maximum limit[1-4]. In these areas US army stored herbicides during the Ranch Hand operation (1962-1971). The remarkable characteristic of dioxin pollution from herbicides is very high percentage of 2,3,7,8-TCDD in comparison with total $TEQ_{PCDDs/PCDFs}$, usually over 93% and even approximately 100%[4-6]. The spreading of dioxin from hotspot areas to surroundings mainly follows the water flow[7]. Low pH level of the soil and also some substances well dissolved in water facilitate the dissolution capacity and spreading of dioxin. With the purpose of using activated carbon to reduce the spreading of pollutants, we studied the adsorption isotherms, evaluated the PCDDs/PCDFs adsorption capacity and rule on activated carbons in different conditions. The experiment was carried out on activated carbons H2, BAU-A, AX21 at different pH 4.0, 7.0, 10.0; different temperature 15 °C, 25 °C, 35 °C and PCDDs/PCDFs solutions with different initial concentration. The extract of dioxin heavily-contaminated soil sampling from Da Nang airport is dissolved in mixture of water and acetone (ratio 96:4, according to v/v) and in hexane in order to have the studied solution bearing remarkable characteristic of dioxin pollution in hotspot areas. The activated carbons very well adsorbed congeners PCDDs/PCDFs. The adsorption effect achieved from 71.1 to 99.9% of total $TEQ_{PCDDs/PCDFs}$ as well as 2,3,7,8-TCDD and TCDDs, from 48.4 to 97.4% of other congeners such as TCDFs, PeCDDs, PeCDFs, OCDD. The Freundlich isothermal equation matches with experimental statistics, the correlation coefficient is very high, within 0.91 - 0.99.

Materials and methods

Activated carbons

Wood-based activated carbon H2 (Vietnam), wood-based activated carbon BAU-A and AX21 (imported) were selected for the study. The activated carbons H2, BAU-A were grinded and sieved to produce different particle sizes. They were washed, dried, kept in tight condition before the experiment[5]. Activated carbon AX21 with fine powder, particle size 0.2 mm has been recommended to apply in the method US.EPA8290 to separate PCDDs/PCDFs from matrices of environmental samples[8].

Preparation of PCDDs/PCDFs solutions

In practice, using PCDDs/PCDFs standards in study is extremely limited. Commercial standards are very expensive which were prepared to produce solution with low concentration in 1.2 ml ampoule. In the single standard, the highest concentration is 50 µg/ml and in the mixture of 17 congeners, the concentration is lower. Therefore, preparing PCDDs/PCDFs sample for the experiment is extremely significant, both having a big quantity of "standard sample" with the concentration suitable for the experiment and ensuring the characteristics of dioxin pollution in the hotspots of Vietnam. Congeners PCDDs/PCDFs were extracted from the dioxin heavily-contaminated soil sampling in the surface layer from the hotspot in Danang airport[5]. Preparing procedure was carried out as US.EPA8280A method, except the addition of isotope-labeled standards[9]. Depending on the purpose, we got research solutions with the different concentration in different media. The experimental solutions were prepared in water with different pH at 4.0, 7.0, 10.0 and total $TEQ_{PCDDs/PCDFs}$ concentration 20, 40, 60, 80, 100, 120, 140 µg/l respectively. In hexane the solutions have total $TEQ_{PCDDs/PCDFs}$ concentration 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 µg/l respectively.

Adsorption isotherms of PCDDs/PCDFs in water on activated carbons H2, BAU-A and AX21

In order to evaluate PCDDs/PCDFs adsorption capability in water on three kinds of activated carbons, we have carried out adsorption isotherms experiments. We selected particle size of 0.25-0.5 mm for H2 and BAU-A. For

AX21, particle size of 0.2 mm of the producer, is used for the experiments. Weighting exactly 5±0.1 mg of each activated carbon and putting it into each vessel which contained 25 ml of experimental solution. The ratio of activated carbon and solution is 1 : 5000. The vessels were shaken by temperature-controlled shaker within 4 hours with the speed of 200 r/min. The influence of pH on PCDDs/PCDFs adsorption capability on activated carbons was examined at pH 4.0, 7.0, 10.0; temperature is unchangeable at 25 °C. The influence of temperature was examined on Vietnamese activated carbon H2 at 15 °C, 25 °C, 35 °C; pH was unchangeable at 7.0.

Adsorption isotherms of PCDDs/PCDFs in hexane on activated carbon AX21

Hexane is a non-polar organic solvent, well diluted congeners PCDDs/PCDFs. In analytical methods, hexane is used for dissolving sample extract before cleanup and compressing through activated carbon column. The adsorption isotherms experiments in hexane were carried out similarly as in water, except the influence of pH.

Analysis of PCDDs/PCDFs and statistics processing

Filter to eliminate activated carbons, obtaining the solutions and preparing for analysis[5]. Confirm and determine congeners PCDDs/PCDFs by GC/MS[9]. The concentration of congeners PCDDs/PCDFs in solution at the equilibrium was C (µg/l). From that, determined adsorbed amount a (µg/l) of congeners PCDDs/PCDFs, total $TEQ_{PCDDs/PCDFs}$ on the activated carbons. In order to evaluate PCDDs/PCDFs adsorption capability, experimental statistics were treated by Freundlich isothermal equation $a = K_F.C^{1/n}$. In this fomular, K_F is the Freundlich constant demonstrating the adsorption capability, n is constant which is specific for the interaction of system. When the interaction force of system is big, value of n will be high. K_F and n are determined basing on the linear dependence of ln a according to ln C.

Results and Discussion

Influence of pH on PCDDs/PCDFs adsorption capability on activated carbons

Congeners PCDDs/PCDFs adsorption isotherms and linear Freundlich isotherms obtained from the experimental statistics. The $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on activated carbons at different pH were illustrated in figure 1 and the previous article[5]. Figure 2 compares the adsorption isotherms on activated carbon H2, BAU-A, AX21 at each pH. The result showed that the Freundlich isotherm equation is suitable for the experimental statistics. This demonstrated by the correlation coefficient (r^2). Value of r^2 was very high, within 0.91-0.99. The influence of pH on adsorption parameters K_F and n was indicated in table 1.

Figure 1: $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on activated carbon H2 at different pH (in form of exponential function and Freundlich linear)

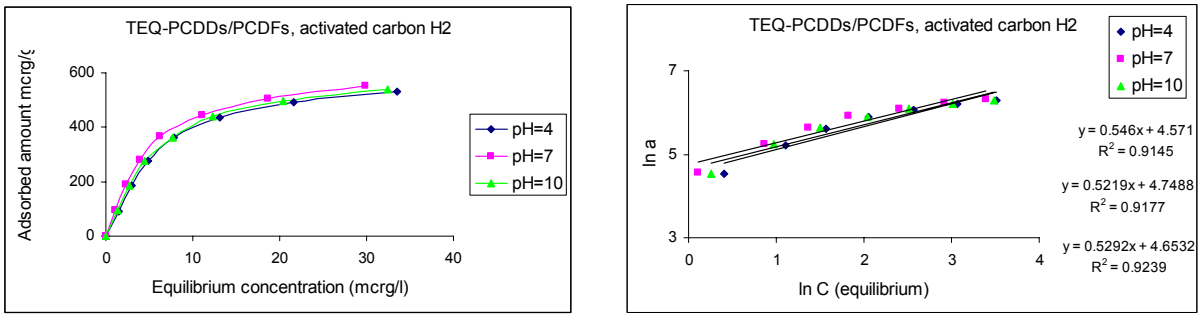
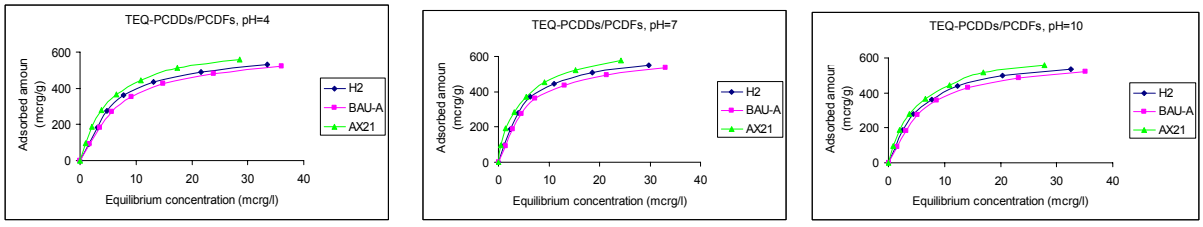


Figure 2: $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on activated carbons H2, BAU-A, AX21 at different pH



In general, at all levels of pH, the PCDDs/PCDFs adsorption capability on three kinds of activated carbons is nearly the same. However, we can see that the adsorption capability of total $TEQ_{PCDDs/PCDFs}$ and also TCDDs on activated carbons at pH = 7.0 is the highest, lower than that at pH = 10.0 and lowest at pH = 4.0. On the contrary, for the congeners TCDFs, PeDCFs, PeCDDs, OCDD, the adsorption capability of the activated carbons is higher at pH = 4.0 and inappreciably lower at other levels of pH. Comparison of adsorption capacity on activated carbons showed that AX21 is the highest, BAU-A is the lowest, H2 is higher than BAU-A. These remarks are clearly indicated by the parameters K_F and n. The values of K_F and n for the total $TEQ_{PCDDs/PCDFs}$ and TCDDs at pH=7.0 > pH=10.0 > pH=4.0. For TCDFs, PeCDFs, PeCDDs, OCDD at pH=4.0 ≥ pH=7.0 ≥ pH=10.0. The values of K_F, n of activated carbon-PCDDs/PCDFs systems for total $TEQ_{PCDDs/PCDFs}$ and also other congeners are arranged as follows: AX21 > H2 > BAU-A. The initial concentration of the congeners are different resulting the different adsorption capability on the activated carbons that means the values of K_F and n are different. The higher initial concentration is the higher K_F and n and vice versa.

Table 1: Dependence on pH of adsorption parameters

pH	H2		BAU-A		AX21		H2		BAU-A		AX21	
	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n
	$TEQ_{PCDDs/PCDFs}$						PeCDFs					
4.0	96.6	1.83	85.6	1.79	121	1.95	8.00	2.00	7.12	1.79	9.06	2.07
7.0	116	1.92	102	1.88	154	2.17	7.21	1.89	6.73	1.68	8.11	1.92
10.0	105	1.89	93.6	1.85	124	1.97	7.17	1.58	6.34	1.56	8.07	1.76
	TCDDs						PeCDDs					
4.0	99.7	1.83	79.5	1.76	128	1.97	3.42	1.72	3.40	1.57	4.24	1.77
7.0	119	1.92	89.6	1.80	163	2.17	3.30	1.66	3.25	1.51	4.20	1.74
10.0	100	1.91	84.5	1.78	132	1.98	2.98	1.64	2.89	1.50	4.16	1.73
	TCDFs						OCDD					
4.0	11.5	1.64	11.0	1.64	14.1	1.90	12.0	1.68	11.8	1.67	13.4	1.76
7.0	11.5	1.60	9.70	1.58	13.7	1.89	11.5	1.61	11.4	1.52	12.7	1.71
10.0	9.75	1.48	8.87	1.47	12.7	1.85	11.3	1.50	11.1	1.49	12.4	1.65

PCDDs/PCDFs adsorption capability on the activated carbons has relationship with their structural parameters. The values such as surface area, capillary volume of AX21 are biger than those of H2, and lower in BAU-A.

Influence of temperature on PCDDs/PCDFs adsorption capability on activated carbons

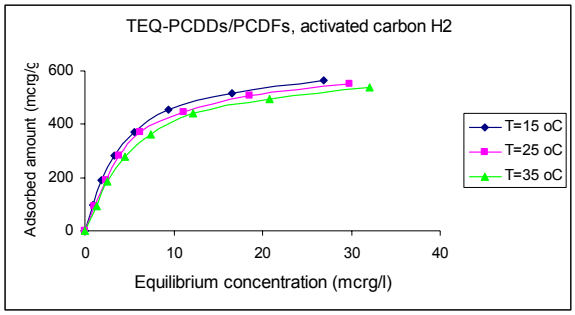
Figure 3 illustrates $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on the selected activated carbon namely H2 at different temperature. The influence of temperature on adsorption parameters K_F and n for congeners PCDDs/PCDFs on H2 was indicated in table 2. Within the studied temperatures from 15 °C to 35 °C, when temperature is increased, K_F and n of activated carbon-PCDDs/PCDFs systems PCDDs/PCDFs decreased. That means PCDDs/PCDFs adsorption capability on activated carbon decreased, it is proved that this adsorption process is physical adsorption. As adsorption is radiation process, the increase of temperature will decrease the system interaction resulting in reduction of adsorption capability.

Influence of solvent on PCDDs/PCDFs adsorption capability on activated carbon

Figure 4 illustrates $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on selected activated carbon namely AX21 in aqueous-acetone solution and in hexane. Influence of the solvent on adsorption parameters K_F and n for congeners PCDDs/PCDFs was indicated in table 3. In hexane medium, PCDDs/PCDFs adsorption capability on activated carbon is higher than that in water. K_F and n of activated carbon-PCDDs/PCDFs systems are higher than those in aqueous-acetone. For $TEQ_{PCDDs/PCDFs}$, TCDDs, the values of K_F and n are 2,2-2,9 times higher. For TCDFs, PeCDFs, PeCDDs, OCDD, they are 1,3-2,2 times higher. May be, functional groups on activated carbon surface

affected the PCDDs/PCDFs adsorption capability in water and diffusibility of PCDDs/PCDFs in capillary resulting in decreasing adsorption capability in water in comparison with that in hexane.

Figure 3: $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on activated carbon H2 at different temperature



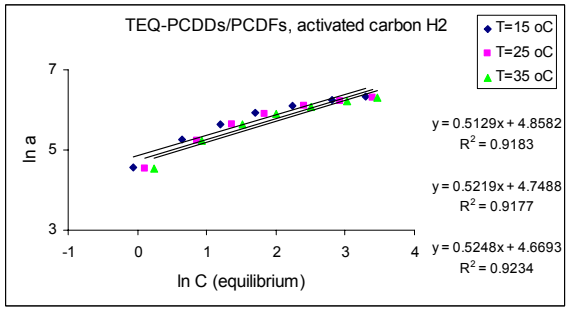
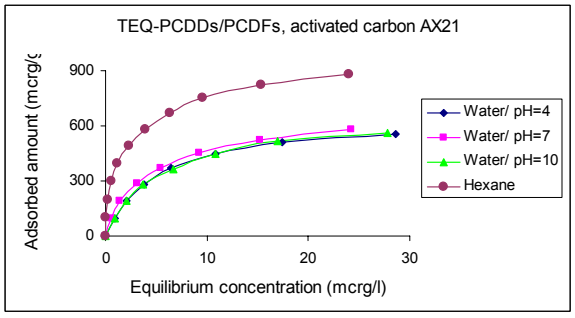


Table 2: Dependence on temperature of adsorption parameters (activated carbon H2 - PCDDs/PCDFs system)

Temperature	$TEQ_{PCDDs/PCDFs}$		TCDDs		TCDFs		PeCDFs		PeCDDs		OCDD	
	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n
15 °C	129	1.95	142	2.06	12.5	1.76	7.59	2.01	3.38	1.69	12.2	1.65
25 °C	115	1.92	119	1.92	11.5	1.60	7.21	1.89	3.30	1.66	11.5	1.61
35 °C	107	1.91	109	1.91	10.9	1.59	6.98	1.81	3.27	1.64	11.0	1.60

Figure 4: $TEQ_{PCDDs/PCDFs}$ adsorption isotherms on activated carbon AX21 in water and in hexane



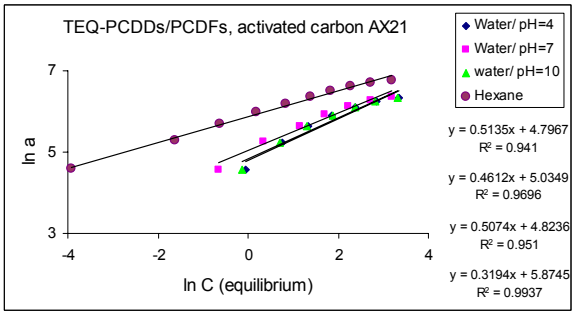


Table 3: Dependence on solvent of adsorption parameters (activated carbon AX21 - PCDDs/PCDFs system)

Medium	$TEQ_{PCDDs/PCDFs}$		TCDDs		TCDFs		PeCDFs		PeCDDs		OCDD	
	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n	K_F	n
Water/ pH = 4.0	121	1.95	128	1.97	14.1	1.90	9.06	2.07	4.24	1.77	13.4	1.76
Water / pH = 7.0	154	2.17	163	2.17	13.7	1.89	8.11	1.92	4.20	1.74	12.7	1.71
Water / pH=10.0	124	1.97	132	1.98	12.7	1.85	8.07	1.76	4.16	1.73	12.4	1.65
Hexane	356	3.13	362	2.89	28.4	2.02	15.4	2.10	7.03	1.83	16.8	2.02

Evaluation of PCDDs/PCDFs adsorption effect from solution on activated carbons

The effect of PCDDs/PCDFs adsorption on activated carbon AX21 from aqueous solution and from hexane was presented in table 4, 5; and on activated carbons H2, BAU-A was presented in the previous article[5]. The experimental results showed that the activated carbons H2, BAU-A and AX21 all very well adsorbed congeners PCDDs/PCDFs in solution. In water, the adsorption effect achieved 71.1-97.4 % of total $TEQ_{PCDDs/PCDFs}$ as well

as 2,3,7,8-TCDD, TCDDs; and 48.4-91.3 % of TCDFs, PeCDDs, PeCDFs and OCDD. Similarly, in hexane, the adsorption effect on activated carbons achieved 87.9-99.9 % and 76.9-97.4 %. Thus, activated carbon H2 manufactured by Vietnam is completely suitable for the purpose of dioxin-contaminated water treatment.

Table 4: Effect of PCDDs/PCDFs adsorption (%) on activated carbon AX21 in aqueous solution

Initial TEQ Con.	TEQ	2378TCDD	TCDDs	TCDFs	PeCDDs	PeCDFs	OCDD
pH=4.0							
20	95.2	95.2	95.3	91.2	87.5	91.3	91.2
40	94.7	94.7	94.7	89.4	84.1	88.7	89.9
60	93.6	93.6	93.6	86.4	82.2	83.9	86.8
80	91.9	91.9	91.9	82.2	79.6	80.1	83.9
100	88.8	88.8	88.8	78.8	74.8	75.2	81.0
120	85.5	85.5	85.5	75.1	71.1	70.8	78.4
140	79.3	79.3	79.3	70.5	65.9	66.4	74.3
pH=7.0							
20	97.4	97.4	94.9	91.1	86.9	88.4	90.1
40	96.5	96.5	93.8	88.3	82.5	82.5	88.4
60	94.8	94.8	92.7	85.6	80.4	79.6	84.3
80	93.2	93.2	91.1	81.4	77.4	74.7	82.1
100	90.8	90.8	88.3	77.7	74.7	71.3	79.5
120	87.3	87.3	84.1	73.9	71.2	66.9	76.9
140	82.7	82.7	78.8	70.2	64.3	62.8	73.1
pH=10.0							
20	95.6	95.6	95.7	88.8	84.5	85.7	88.8
40	94.9	94.9	94.9	87.3	83.6	79.8	86.4
60	93.8	93.8	93.8	83.5	81.1	76.2	83.7
80	91.7	91.7	91.7	79.7	77.4	73.9	81.7
100	89.1	89.1	89.1	75.1	73.9	70.5	78.9
120	85.9	85.9	85.9	71.5	69.5	66.5	75.7
140	80.1	80.1	80.1	67.9	63.2	61.6	71.5

Table 5: Effect of PCDDs/PCDFs adsorption (%) on activated carbon AX21 in hexane

Initial TEQ Con.	TEQ	2378TCDD	TCDDs	TCDFs	PeCDDs	PeCDFs	OCDD
20	99.9	99.9	99.8	97.4	90.5	91.6	89.8
40	99.5	99.5	99.4	97.0	90.2	91.3	89.7
60	99.1	99.1	99.1	96.4	89.8	90.4	89.5
80	98.5	98.5	98.4	95.4	89.1	89.5	88.9
100	97.7	97.7	97.7	94.4	87.9	88.9	88.1
120	96.7	96.7	96.6	93.0	86.7	87.1	86.5
140	95.5	95.5	95.5	91.0	85.3	85.5	84.9
160	94.0	94.0	93.9	88.5	83.7	83.9	82.8
180	91.0	91.0	90.9	86.0	80.9	80.5	80.3
200	88.0	88.0	87.9	83.5	77.3	77.1	76.9

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