REMOVAL OF PCDDs/PCDFs FROM SOLUTION BY USING ACTIVATED CARBONS - ADSORPTION KINETICS SURVEY

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Introduction

Activated carbon is widely applied to eliminate pollutants in drinking water, waste water, air, exhaust fume, pharmaceutical products, drinks, foodstuff. Many kinds of activated carbons have been studied by international authors to eliminate PCDDs/PCDFs and dioxin-like PCBs from fish oils, vegetable oils, flue gases, emission of incinerators, metallurgical furnace[1-9]. In Vietnam, at the hotspot areas, where US army used to store herbicides during the Ranch Hand operation which have dioxin-contaminated level many times higher than acceptable maximum level[10-13]. From that areas the spreading of pollutants to surroundings mainly follows the water flow. Some researches has been carried out to reduce spreading of dioxin using activated carbons as adsorption material[14-17]. With the aim of using Vietnamese activated carbons to eliminate and minimize the spreading of dioxin in water, we have research PCDDs/PCDFs adsorption kinetics on the selected wood-based activated carbon namely H2. The influences of initial concentration, temperature, pH, particle size parameters on the adsorption velocity have been surveyed and compared with imported activated carbons BAU-A, AX21. After 4 hours, activated carbon H2 removed over 84.3% of congeners PCDDs/PCDFs in water. The adsorption effect is equivalent to expensive imported activated carbons. And, it is completely suitable for water treatment purpose.

Materials and methods

Activated carbons

We continue to select domestic activated carbons H2, imported activated carbons BAU-A and AX21 for this survey basing on previous study with nine types of activated carbons[14]. H2 and BAU-A are wood-based activated carbons, were grinded and sieved to produce the different particle sizes: 0.074-0.1 mm, 0.25-0.5 mm, 0.76-1 mm. AX21 in fine powder, particle size 0.2 mm has been recommended for using in dioxin analysis.

PCDDs/PCDFs solution

PCDDs/PCDFs solution is prepared by extracting from dioxin heavily-contaminated soil sampling at the hotspot in Danang airport[16]. The experimental solutions with $TEQ_{PCDDs/PCDFs}$ concentration were 40, 80, 120 µg/l diluting in mixture of bidistilled water and acetone with ratio of 96 : 4 by v/v (following abbreviated as water), which adjusted pH at 4.0, 7.0, 10.0. This solutions added 4% acetone to ensure the complete dissolution of PCDDs/PCDFs. The experimental solutions in hexane prepared with $TEQ_{PCDDs/PCDFs}$ 60, 120, 180 µg/l.

Adsorption kinetics experiments of PCDDs/PCDFs in water

In order to survey the PCDDs/PCDFs adsorption velocity in water, we have carried out adsorption kinetics experiments on activated carbons H2, BAU-A and AX21. The experimental amount of each activated carbon was 20±0.1 mg, particle size was 0.25-0.5 mm for H2 and BAU-A. For AX21, used original particle size 0.2 mm. The experimental solutions had volume of 100 ml. The ratio of activated carbon and solution was 1: 5,000. The experiments was carried out on temperature-controlled shaker at speed of 200 r/min. The influence of initial concentration on adsorption velocity was surveyed with $TEQ_{PCDDs/PCDFs}$ 40, 80, 120 µg/l, at 25 °C, pH = 7.0. The influence of temperature on adsorption velocity was surveyed at 15 °C, 25 °C and 35 °C, $TEQ_{PCDDs/PCDFs}$ 80 µg/l, pH = 7.0. The influence of pH on adsorption velocity was surveyed at pH = 4.0, 7.0, 10.0, at 25 °C, $TEQ_{PCDDs/PCDFs}$ 80 µg/l. The influence of particle size on adsorption velocity was surveyed at 0.074-0.1 mm, 0.25-0.5 mm, 0.76-1 mm for H2, BAU-A, at 25 °C, $TEQ_{PCDDs/PCDFs}$ 80 µg/l, pH = 7.0.

Adsorption kinetics experiments of PCDDs/PCDFs in hexane

PCDDs/PCDFs adsorption kinetics study in hexane was carried out on AX21. The influence of initial concentration on adsorption velocity was surveyed with $TEQ_{PCDDs/PCDFs}$ 60, 120, 180 µg/l, at 25 °C. The influence of temperature on adsorption velocity was surveyed at 15 °C, 25 °C, 35 °C, $TEQ_{PCDDs/PCDFs}$ 120 µg/l.

Sampling and analyzing congeners PCDDs/PCDFs
After each different period of 0, 2.5, 5, 7.5, 10, 15, 20, 30, 60, 90 minutes and 2, 4, 6, 12, 24, 48 hours, exactly 1 ml of experimental solution was sucked. The solution in water was extracted by hexane. The extract was spiked with ^{13}C-, ^{37}Cl-labeled PCDDs/PCDFs standards and cleaned up[16]. The concentration of congeners PCDDs/PCDFs in the solutions at each sampling time are determined by GC/MS[18]. From that, calculated adsorbed amount a (µg/l) of congeners PCDDs/PCDFs on the activated carbons.

Results and discussion
Evaluation of parameters affecting on PCDDs/PCDFs adsorption velocity in water
The influence of initial concentration, temperature, pH of solution and particle size on PCDDs/PCDFs adsorption velocity on H2 in water was indicated in figures 1, 2, 3, 4. The kinetics diagrams showed that:

Figure 1: Influence of initial concentration, in water

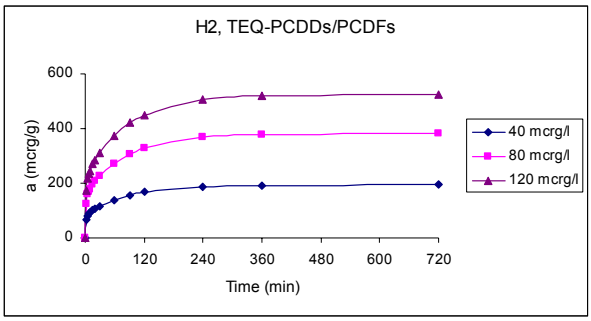


Figure 2: Influence of temperature, in water

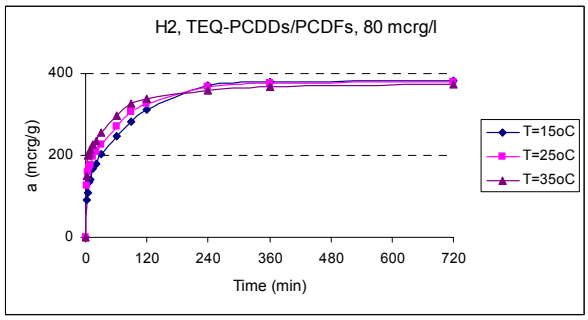


Figure 3: Influence of pH, in water

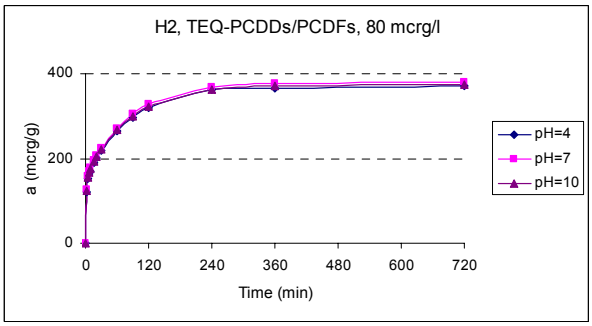
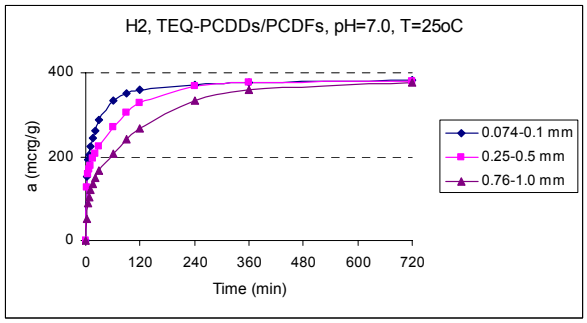


Figure 4: Influence of particle size, in water



The adsorption velocity increases when PCDDs/PCDFs concentration was increased in outside phase. The big difference in initial concentration has increased the amount of congeners transported in particle and pellicle as well. The PCDDs/PCDFs adsorption process on activated carbons is physical adsorption. Therefore, the diffusibility process in particle for systems of PCDDs/PCDFs-activated carbons is at the tendency of volume diffusibility. The adsorption mechanism is filling up the capillaries.

Within interval of surveying temperature, the higher temperature the faster PCDDs/PCDFs adsorption velocity and the quicker system equilibrium was achieved. At equilibrium state, the higher temperature of the system the lower adsorption capacity. The increased temperature increases the thermal motion of molecules which participated in the diffusibility process and decreases the interaction force in the system. Within surveying pH interval, we can see that pH affected insignificantly on the adsorption velocity of systems and adsorption capacity as well.

The influence of particle size on adsorption velocity of the systems was clearly demonstrated. The adsorption velocity increases when the particle size of activated carbon was decreased. For the particle size 0.074-0.1 mm,

adsorption equilibrium obtained after about 90 minutes; particle size 0.25-0.5 mm, after about 240 minutes; and particle size 0.76-1.0 mm, after over 360 minutes. The diffusibility in particle is the slowest step which determine the adsorption velocity. When the particle size is decreased, the adsorption velocity increases as the easier diffusibility process in particle resulting from the decrease of diffusibility distance.

Comparing PCDDs/PCDFs adsorption velocity between activated carbons H2, BAU-A and AX21 was illustrated in figure 5. In general, the adsorption velocity of AX21 > H2 > BAU-A. Therefore, system of PCDDs/PCDFs-AX21 reached the equilibrium state quicker than that of the remaining systems.

Evaluation of parameters affecting on PCDDs/PCDFs adsorption velocity in hexane

The influence of initial concentration, temperature on PCDDs/PCDFs adsorption velocity of AX21 in hexane was demonstrated in figures 6, 7. Comparison of adsorption velocity in water and in hexane was demonstrated in figure 8. The influence of initial concentration, temperature on adsorption velocity of activated carbon in hexane was the same that in water. However, we can easily see the clear difference that the adsorption velocity in hexane is much quicker. The system reached the equilibrium state sooner after only 10 minutes and the adsorption capacity of the system was also more than that in water.

Figure 5: Comparison of adsorption velocity among the activated carbons in water

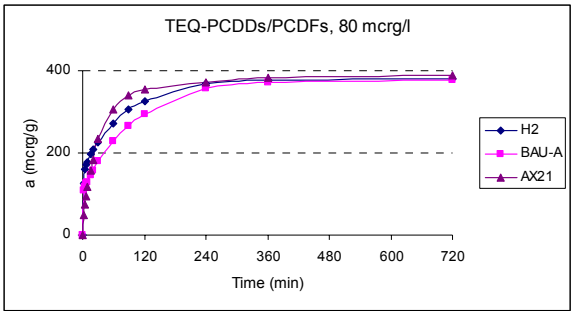


Figure 6: Influence of initial concentration on adsorption velocity of AX21 in hexane

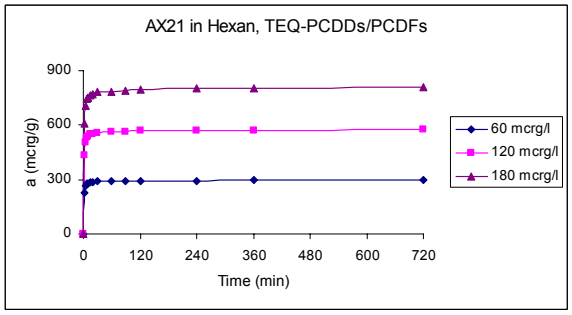


Figure 7: Influence of temperature, in hexane

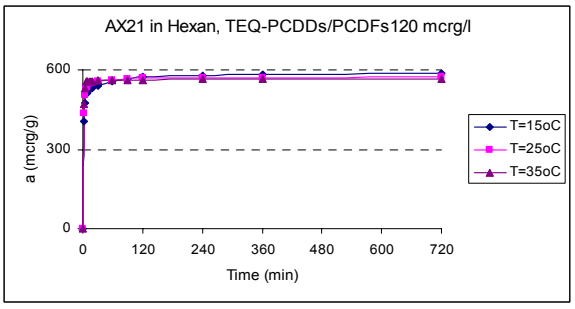
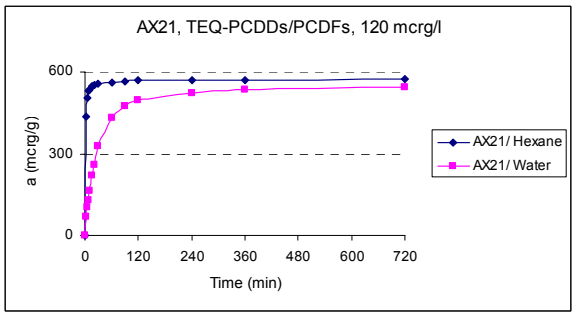


Figure 8: Comparison of adsorption velocity in hexane and in water



Evaluation of PCDDs/PCDFs removal from the solution

Evaluation of PCDDs/PCDFs removal from solution was demonstrated by mean of evaluating adsorption effect of activated carbons at different sampling time in kinetics experiments. The results were presented in table 1. On the experimental conditions in water with initial $TEQ_{PCDDs/PCDFs}$ concentration within 40-120 µg/l, after only 30 minutes H2 removed 51.7-58.0 % of PCDDs/PCDFs; BAU-A removed less (40.8-45.5 %), and AX21 removed more (54.3-60.8 %). After 240 minute experiment, the activated carbons removed 84.3-94.0 %, 81.7-90.9 % and 86.8-96.2 % respectively. This results are completely suitable with the adsorption effect determined in adsorption isotherm experiments after 4 hours. In hexane with initial $TEQ_{PCDDs/PCDFs}$ concentration within 60-180 µg/l (higher than that in water), the process of PCDDs/PCDFs adsorption happened very quickly, nearly immediately.

AX21 removed 67.4-75.9 % of PCDDs/PCDFs after only 2.5 minutes, 86.8-97.0 % after 30 minutes and 88.9-98.2% after 240 minutes.

Table 1: Effect of PCDDs/PCDFs removal from the solutions

Activated carbon	H2	BAU-A	AX21	AX21
Initial concentration (μg/l)	40-80-120	40-80-120	40-80-120	60-120-180
Medium	Water-Acetone	Water-Acetone	Water-Acetone	Hexane
Time (min)	Effect of PCDDs/PCDFs removal (%)			
2.5	28.8 - 32.3	24.5 - 27.3	11.3 - 12.8	67.4 - 75.9
5.0	36.4 - 40.8	27.1 - 30.1	17.0 - 19.1	78.2 - 87.7
7.5	39.0 - 43.7	28.6 - 31.7	21.7 - 24.3	82.4 - 92.3
10	40.8 - 45.6	29.5 - 32.6	27.4 - 30.7	83.2 - 93.2
15	44.8 - 50.2	33.0 - 37.0	36.9 - 41.3	85.2 - 95.2
20	47.4 - 53.2	35.6 - 40.0	43.1 - 47.7	85.8 - 95.8
30	51.7 - 58.0	40.8 - 45.5	54.3 - 60.8	86.8 - 97.0
60	62.0 - 69.4	51.9 - 57.7	72.2 - 80.3	87.4 - 97.6
90	70.1 - 78.2	60.6 - 67.6	79.1 - 88.4	87.8 - 97.9
120	75.1 - 83.9	67.3 - 75.0	82.8 - 91.9	88.6 - 98.0
240	84.3 - 94.0	81.7 - 90.9	86.8 - 96.2	88.9 - 98.2
360	86.7 - 96.4	85.0 - 95.0	88.9 - 97.7	89.0 - 98.5
720	87.1 - 97.3	85.9 - 95.8	90.9 - 98.5	89.9 - 99.1

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