THE CHARACTERISTICS OF DIOXIN POLLUTION IN HOTSPOT AREA AND THE ADSORPTION ISOTHERMS ON THE ACTIVATED CARBONS

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Introduction

It is pointed out in many researches that the dioxin residual levels in hotspot areas in Vietnam[1-4] is much higher than the international acceptable maximum limit. The dioxin pollution in these sites are related using herbicides by US army during the Ranch Hand operation. The spreading of dioxin from hotspot areas to surroundings mainly follows the water flow. The heavily dioxin-contaminated soil is washed with the rain and accumulates at the nearest ditches and reservoirs. The low pH level of soil together with the substances which are easy to dissolve in water, such as, policlophenols, clorophenoxyaxetic, humic acid and much low-molecular-weight organochlorines make water become the solution which can dissolve dioxin and increase the pervasion of dioxin to surroundings. So, it is necessary to determine the characteristics of dioxin pollution in soil, sediment and sludge samples. Soil extract is dissolved in water solution with 4% acetone to make a research solution which carry characteristics of dioxin pollution in hotspot area. Assess the effect and rule of PCDDs/PCDFs' adsorption on the activated carbons by studying adsorption equilibrium (adsorption isotherms) in different conditions. Activated carbons H2 of Vietnam and BAU-A of Russia are selected for this research[5]. Experimental statistics are processed by Freundlich isothermal equation.

Materials and methods

Determine the characteristics of dioxin pollution in hotspot area

The mixed soil sample on the surface layer at the depth of 0-20cm, the sediment and sludge samples in hotspot area that were determined with very high concentration of PCDDs/PCDFs. Soil sample (80g each thimble, 40 times, total 3.2kg) is extracted soxhlet with toluene. Sample extract is condensed and dissolved in hexane, then cleaned up by concentrated H_2SO_4 acid and solutions of NaCl 5%, KOH 20%, dried by Na_2SO_4. The extract is cleaned up by the multilayers column with silica, silica impregnated in 40% of concentrated H_2SO_4, silica impregnated in 20% of KOH and Na_2SO_4. PCDDs/PCDFs fraction is separated from the AX21 activated carbon and the neutral Al_2O_3 columns. The sediment and sludge samples with amount of 20g are performed correlatively. For cross-check, these samples are also analyzed in Japan, Russia and Sweden.

Determine the characteristics of dioxin pollution in hotspot area base on the concentration of PCDDs/PCDFs in the received final fractions.

Research adsorption isotherms of dioxin on the activated carbons

Prepare the stock solution of PCDDs/PCDFs

Evaporate solvent in the final PCDDs/PCDFs fraction of soil sample, then dissolve in acetone. Add the equal known volume of this solution to three vessels. Evaporate acetone reach to 0.1ml, then dissolve in mixture of bidistilled water and 4% acetone with difference pH at 4.0, 7.0 and 10.0. Concentration of PCDDs/PCDFs in stock solutions is determined at 100ngWHO-TEQ/ml.

Prepare the activated carbons

The wood-based activated carbons are chosen for purpose of this research. Activated carbon H2 made in Vietnam and BAU-A made in Russia. Activated carbons are ground and sifted to select difference particle sizes. Wash with bidistilled water reach to neutral pH and reject dust, dry at 110°C during three hours and preserve before experiment.

The adsorption equilibrium experiments
Add in turn 5, 10, 15, 20 and 25ml stock solutions of PCDDs/PCDFs into the difference vessels, each one has previous 20, 15, 10, 5 and 0ml bidistilled water with 4% acetone at correlative pH at 4.0, 7.0, 10.0. The received research solutions have 25ml of volume, the correlative concentration at 20, 40, 60, 80, 100ng WHO-TEQ/ml.

Take exactly 5mg of each activated carbon at the particle size of 0.25-0.5mm and put into each of vessels containing the research solution. The ratio of activated carbon and solution is 1: 5000. The adsorption equilibrium experiments are shaken continually for 4 hours at the speed of 200 rounds per minute and the temperature of 20±0.3°C. Filter out activated carbon. Take the solution, add ^{13}C-isotope labeled standards of PCDDs/PCDFs. Extract by shaking 3 times, each time with 15ml hexane in 15 minutes, 200 rounds per minute. The extract is cleaned up and separated the PCDDs/PCDFs fraction. Determine equilibrium concentration of PCDDs/PCDFs in the solution by GC/MS[6].

Results and discussions

Characteristics of dioxin pollution in hotspot area

The figure 1 illustrates the characteristics of dioxin pollution in soil on the surface layer at the depth of 0-20cm (the surface soil), in sediment at treatment basin and sludge at the lake in hotspot area in Da Nang. According to the received data, the dioxin residual levels in soil, sediment and sludge still exceed many times than the international acceptable maximum limit (1ppb). The cross-check samples that were tested by the international laboratories also show the same results, the concentration of all congeners are rather suitable to each other[7,8]. The mainly component of dioxin pollution is 2,3,7,8-TCDD with very high concentration, it occupies over 93% of total TEQ. This rate is much higher than of the sources that release dioxin in the industry or the other ones. This shows that the original source of dioxin pollution in hotspot areas is related with herbicides used by US army during the war. This comment is quite suitable to the researches of Vietnam as well as international[3,4].

According to the direction of water flow, the dioxin residual levels decrease. The concentration of 2,3,7,8-TCDD and total TEQ in the surface soil is much higher than in sediment, and in sediment is much higher than in sludge. However, the concentration of congeners HpCDD, OCDD and OCDF increases. Of OCDD and OCDF in sediment and sludge is 5-7 times higher than in surface soil, but of HpCDD is 13-23 times higher than one. There is not the quite difference with the concentration of other congeners in these samples. The concentration change between 2,3,7,8-TCDD and other congeners may according to the difference of their durability in soil, sediment and sludge. And also note that beside the accumulation of dioxin contaminated soil from hotspot, there is the soil from other area so it takes the change in concentration and makes the difference with congeners in the characteristics of dioxin pollution.

Effect and rule of dioxin adsorption on activated carbon

Tables 1 and 2 show that in the same experimental condition, at all of different concentrations and pH, the ability of dioxin adsorption (total TEQ, congeners, isomers) on activated carbon H2 is higher than BAU-A. In accordance with TEQ, the adsorption effect on H2 is about 86.3% to 97.3% and 92.1% in average, and on BAU-A is a little lower, about 84.2% to 93.0% and 90.2% correlatively. The adsorption ability for each congener or isomer on activated carbons is different. The best adsorption occurs with 2,3,7,8-TCDD and isomers of TCDDs, and lower with the other congeners. The amount of adsorbed congener increases with the concentration of research solution, especially, the most toxicant 2,3,7,8-TCDD and total TCDDs increase near-linearly. As a result, at all experiments the adsorption effect in percentage is different only 6.2% to 6.8% with H2 and 6.8% to 7.7% with BAU-A. With other congeners, the adsorption effect in percentage is different quite much. In a form manner, it decreases when the concentration of research solution increases, especially, in BAU-A.

To assess the ability of dioxin adsorption from water solution on the activated carbons, experimental statistics are also processed by Freundlinch isothermal equation: $a = K_F.C^{1/n}$. In this formula, a is the concentration of adsorbed congener (μg/g); C is the congener concentration in solution at equilibrium (μg/l); K_F is Freundlich constant, n is constant which is specific for the interaction of system. K_F and n are determined from the linear dependence of lna from lnC. The result showed that Freundlich isothermal equation matches with experimental

statistics. This can be drawn from the values of correlation coefficient (r^2). The figure 2 illustrates the dioxin (total TEQ) adsorption isotherms obtained with H2 and BAU-A at different pH, at 20°C. The values r^2 are around 0.92-0.99.

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Figure 1: Characteristics of dioxin pollution in hotspot area

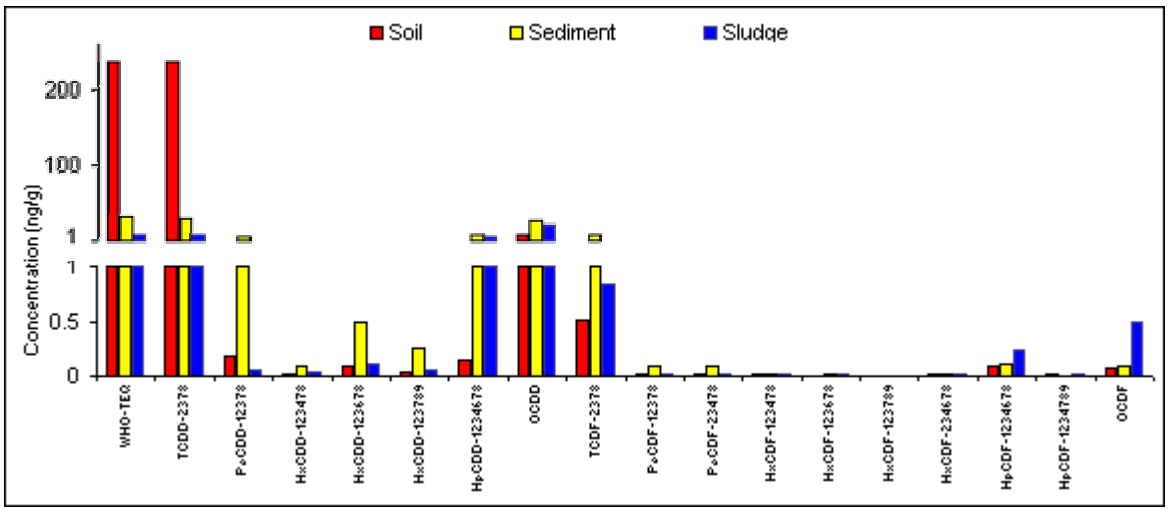
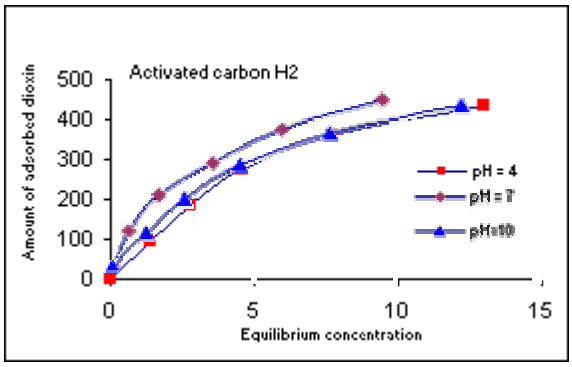


Figure 2: Dioxin (total TEQ) adsorption isotherms on activated carbons H2 and BAU-A



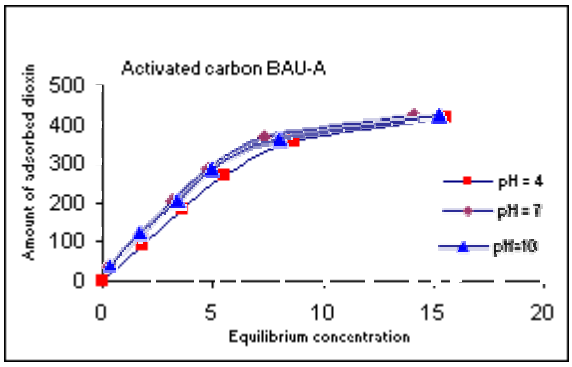


Table 1: Effect of dioxin adsorption (%) on activated carbon H2

Initial Conc. (TEQ)		TEQ	2378TCDD	ΣTCDD	ΣTCDF	ΣPeCDD	ΣPeCDF	OCDD
pH = 4	20	92.5	92.5	93.0	95.6	86.0	94.8	87.9
	40	92.2	92.2	92.3	89.9	77.0	86.2	86.7
	60	92.0	92.0	91.9	88.3	72.1	82.6	84.7
	80	90.2	90.2	89.2	83.5	72.1	78.7	80.0
	100	86.3	86.3	86.1	82.7	66.3	77.8	77.3
pH = 7	20	97.3	97.3	96.3	87.3	80.0	86.7	86.2
	40	96.0	96.0	93.8	81.1	75.6	80.0	85.3
	60	94.1	94.1	92.7	79.5	66.3	76.9	84.7
	80	92.5	92.5	91.1	73.0	60.0	68.6	80.2
	100	90.5	90.5	90.3	72.2	52.2	68.2	76.7
pH =10	20	93.9	93.9	92.0	77.6	65.0	72.7	83.1
	40	93.7	93.7	90.8	74.4	63.6	71.2	82.9
	60	92.5	92.5	91.4	70.9	60.0	68.7	81.9
	80	90.4	90.4	87.0	67.9	59.1	68.2	81.7
	100	87.7	87.7	83.8	60.3	51.9	60.0	76.8

Table 2: Effect of dioxin adsorption (%) on activated carbon BAU-A

Initial Conc. (TEQ)		TEQ	2378TCDD	ΣTCDD	ΣTCDF	ΣPeCDD	ΣPeCDF	OCDD
pH = 4	20	91.0	91.0	89.5	83.0	70.0	80.8	87.3
	40	90.7	90.7	88.7	82.2	69.7	76.9	86.5
	60	90.8	90.8	88.0	73.9	69.2	70.1	84.3
	80	89.1	89.1	87.4	72.0	66.7	67.0	84.1
	100	84.2	84.2	81.2	63.4	59.1	61.2	80.9
pH = 7	20	93.0	93.0	91.4	78.8	60.0	75.8	83.8
	40	92.8	92.8	88.9	70.2	55.0	69.7	83.0
	60	92.3	92.3	88.4	68.5	53.7	66.3	80.2
	80	91.0	91.0	87.1	66.8	52.4	62.9	79.4
	100	85.9	85.9	84.3	57.3	50.0	56.4	77.7
pH=10	20	92.5	92.5	90.2	75.0	45.0	76.6	70.0
	40	92.3	92.3	87.4	71.2	43.5	70.0	68.3
	60	92.2	92.2	87.0	69.5	43.3	63.2	58.9
	80	90.3	90.3	86.2	69.0	42.9	62.4	58.3
	100	84.8	84.8	82.1	50.6	37.8	52.5	58.0